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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

04100365.8

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Functionalized photoinitiators

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Functionalized photoinitiators

The present invention relates to novel derivatives of alpha-aminoketones, to their use as photoinitiators for the photopolymerization of ethylenically unsaturated compounds and to their use to prepare multifunctional photoinitiators.

Alpha-aminoketone compounds are well known photoinitiators. Commercially available is for Example Irgacure 369® and Irgacure 907®.

Derivatives of alpha-aminoketones, which have an amino group in the 4-position of the phenyl radical are described, for example, in EP0 138 754 A2.

The European Patent Publication EP 284561 B1 describes photoinitiators of the formula $Ar\text{-}CO\text{-}C(R_1R_2)\text{-}N(R_3R_4)$ or $Ar\text{-}CO\text{-}C(R_1R_2)\text{-}X\text{-}C(R_1R_2)\text{-}CO\text{-}Ar$ or $Ar\text{-}CO\text{-}C(R_1NR_3R_4)\text{-}Y\text{-}C(R_1NR_3R)\text{-}CO\text{-}Ar$, wherein Ar is e.g. phenyl optionally substituted by NR_7R_8.

The European Patent Publication EP 1 357 117 A2 describes novel aminoketone derivatives, obtainable by reacting 1-{4-[bis-(2-hydroxy-ethyl)-amino]}-2-methyl-2-morpholino-1-propanone or 2-(dimethylamino)-1-{4-[(2-hydroxyethyl)methylamino]-phenyl}-2-phenylmethyl-1-butanone with ε-caprolactone.

The US Patent 6 022 906 describes photoinitiators of the formula $Y\text{-}X\text{-}Ar\text{-}CO\text{-}C(R_1R_2)\text{-}N(R_3R_4)$ provided that at least one of the radicals is substituted by SH. These photoinitiators are prepared using, for example, 1-[4-(3-Hydroxypropylamino)phenyl]-2-dimethylamino-2-benzyl-propan-1-one or 1-[4-(3-Hydroxypropylamino)phenyl]-2-dimethyl-amino-2-benzyl-butan-1-one. These intermediate compounds have not been described as photoinitiators.

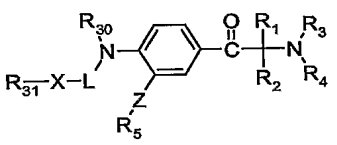
There is an increasing need to minimize the emission of volatile organic components before curing and to minimize the migration and/or extraction of residual photoinitiator components from the cured product, while maintaining high initiator efficiency. For example, inks used in printing on plastics food packaging should ideally meet the standards for minimization of extractable compounds from the coated and/or printed plastics. Such contamination can

cause problems of taint and odor of the foodstuff. Moreover, for other coating compositions, it is important to minimize migration of reactive materials, which may cause other undesirable effects such as loss of adhesion to the substrate or yellowing.

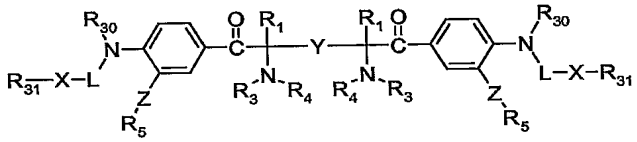
One approach is to use photoinitiators of increased molecular size to reduce the level of migratable and/or extractable residual photoinitiator components in a cured coating or ink composition. Such polymeric photoinitiators are, for example, disclosed in EP0 161 463 A1 and include a commercially available compound, Fratelli-Lamberti's KIP 100.
However, polymeric photoinitiators are often high viscose, which makes the handling difficult.

It has been found that low odor - low migration-photoinitiators can be obtained by using photoinitiators having a suitable reactive group.

The invention relates to novel photoinitiators of formula I or II



I



II

wherein

L is a linker;

X is -O-, -S- or -NR_{32}-;

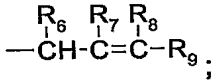
Y is a direct bond, C_1-C_{16}-alkylene, cyclohexylene, xylylene, dihydroxyxylylene, C_4-C_8-alkenediyl, C_6-C_{10}-alkadienediyl or dipentenediyl;

Z is a direct bond, -CH_2-, -O-, -S- or -NR_{10}-;

R_1 and R_2 are independently of each other either

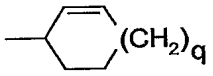
(a) linear or branched C_1-C_{12}-alkyl, which is unsubstituted or substituted by one or more of the groups C_1-C_4-alkyoxy, phenoxy, halogen or phenyl;

(b) a radical of the formula



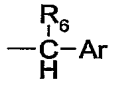
;

(c) a radical of the formula



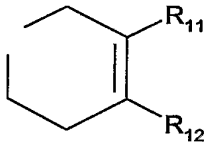
where q is 0, 1, 2 or 3; or

(d) a radical of the formula

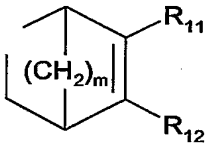


where Ar is phenyl, which is unsubstituted or substituted by one or more of the groups halogen, OH, NO_2, $-N(R_{10})_2$, C_1-C_{12}-alkyl, C_1-C_4-alkyl that is additionally substituted by OH, halogen, $N(R_{10})_2$, C_1-C_{12}-alkoxy, $-COO(C_1$-C_{18}-alkyl), $-CO(OCH_2CH_2)_nOCH_3$ or $-OCO(C_1$-C_4-alkyl); C_1-C_{12}-alkyoxy, C_1-C_4-alkyoxy that is additionally substituted by $-COO(C_1$-C_{18}-alkyl) or $-CO(OCH_2CH_2)_nOCH_3$; $-OCO(C_1$-C_4-alkyl), C_1-C_8-alkylthio, phenoxy, $-COO(C_1$-C_{18}-alkyl), $-CO(OCH_2CH_2)_nOCH_3$, phenyl or benzoyl; where n is 1-20; or

R^1 together with R^2 forms a ring of the formula



or



where m is 1 or 2;

R_3 is hydrogen, C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, $-COO(C_1$-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl or C_7-C_9-phenylalkyl;

R_4 is C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, $-COO(C_1$-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl; or R_4 and R_2 together is C_1-C_7-alkylene, C_7-C_{10}-phenylalkylene, o-xylylene, 2-butenylene or C_2-C_3-oxa- or azaalkylene; or R_4 and R_3 together is C_3-C_7-alkylene that may be interrupted by -O-, -S-, -CO- or $-N(R_{13})$- and substituted by hydroxy, C_1-C_4-alkoxy or $-COO(C_1$-C_4-alkyl);

R_5 is hydrogen or C_1-C_4-alkyl; or R_5 together with R_{30} is C_1-C_2-alkylene;

R_6 is hydrogen, C_1-C_8-alkyl or phenyl;

R_7, R_8 and R_9 independently of each other are hydrogen or C_1-C_4-alkyl, or R_7 and R_8 together are C_3-C_7-alkylene;

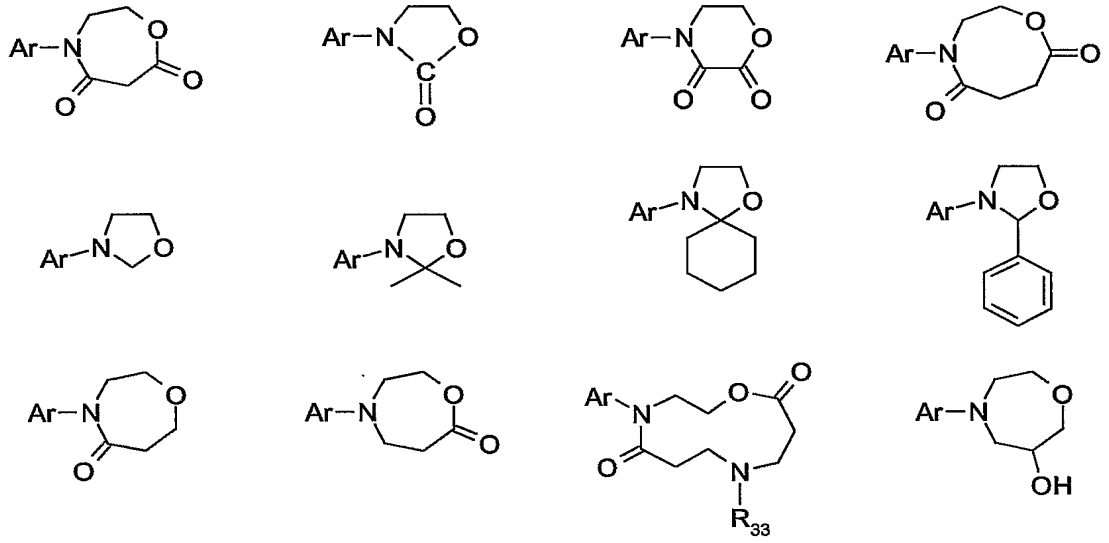
R_{10} is hydrogen, C_1-C_8-alkyl, C_3-C_5-alkenyl, C_7-C_9-phenlyalkyl, C_1-C_4-hydroxyalkyl or phenyl;

R_{11} and R_{12} independently of each other are hydrogen or C_1-C_4-alkyl, or R_{11} and R_{12} together are C_3-C_7-alkylene;

R_{13} is hydrogen, C_1-C_{12}-alkyl, which may be interrupted by one or more -O- or C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, $-CH_2CH_2CN$, $-CH_2CH_2COO(C_1$-C_4-alkyl), C_2-C_8-alkanoyl, or benzoyl;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -$NR_{33}R_{34}$, -SR_{35}, -COOH or -COO(C_1-C_4-alkyl); or benzoyl or norbornenoyl substituted by hydroxy; or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl; or

R_{30} and R_{31} together with the group –N-L-X form cyclic structures selected from



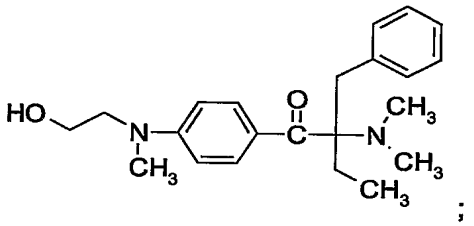
R_{32} is hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); .. C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl benzoyl or norbornenoyl substituted by hydroxy, C_1-C_4-alkoxy, -$NR_{33}R_{34}$, -SR_{35}, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl;

R_{33} and R_{34} independently of one another are hydrogen, C_1-C_{12}-alkyl, C_2-C_4-hydroxy-alkyl, C_3-C_{10}-alkoxyalkyl, C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl, C_2-C_{18}-alkanoyl or benzoyl; or R_{33} and R_{34} together are C_2-C_8-alkylene optionally interrupted by -O-, -S- or -NR_{36}- , or are C_2-C_8-alkylene optionally substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl);

R_{35} is C_1-C_{18}-alkyl, hydroxyethyl, 2,3-dihydroxypropyl, cyclohexyl, benzyl, phenyl, C_1-C_{12}-alkylphenyl, -CH_2-COO(C_1-C_{18}-alkyl), -CH_2CH_2-COO(C_1-C_{18}-alkyl) or -CH(CH_3)-COO(C_1-C_{18}-alkyl);

R_{36} is hydrogen, C_1-C_{12}-alkyl optionally interrupted by one or more no adjacent –O-atoms, C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, -CH_2CH_2CN, -CH_2CH_2COO(C_1-C_4-alkyl), C_2-C_{12}-alkanoyl or benzoyl.

with the proviso that the following compounds are excluded: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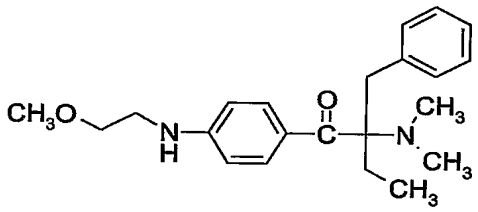
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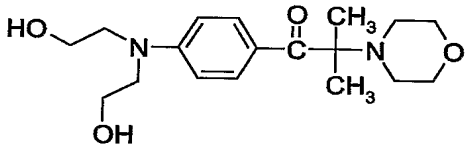
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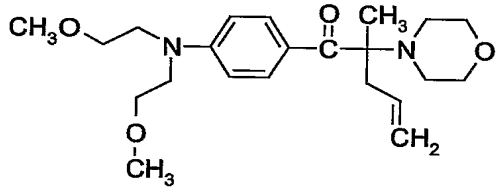
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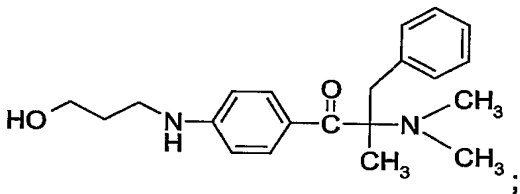
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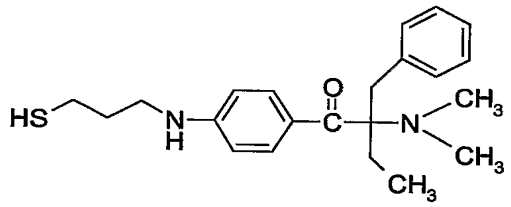
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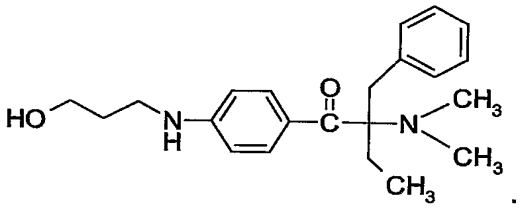
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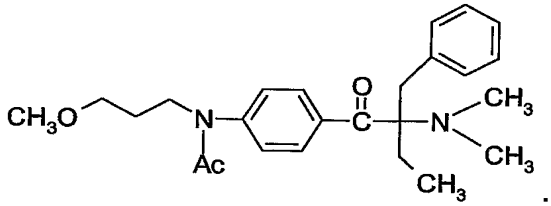
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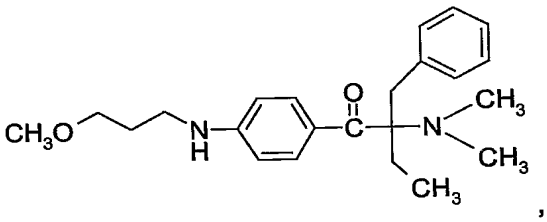
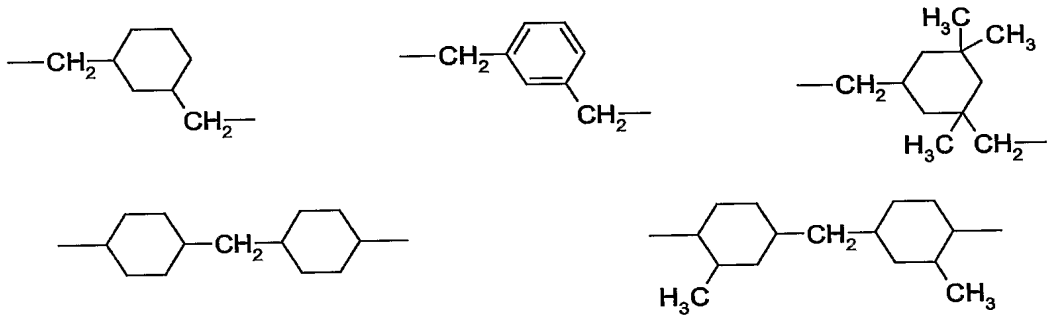


Definitions:

Suitable **linkers** are linear or branched C_2-C_{18}-alkanediyl, or C_2-C_{30}-alkanediyl optionally interrupted by one or more not adjacent O-atoms, and/or optionally substituted by one or more hydroxy atoms. Other suitable linkers are 1,3-cyclohexanediyl, 1,4-cyclohexanediyl, 4-methyl-1,3-cyclohexanediyl or are selected form the following structures.



In the present description the term "alkyl", alone or in combination, signifies a straight-chain or branched-chain alkyl group; the upper and lower limits of the number of carbon atoms is given in each case.

The term "alkoxy", alone or in combination, signifies a group of the formula alkyl-O-in which the term "alkyl" has the previously given significance.

The term "alkenyl", alone or in combination, means a straight-chain or branched-chain hydrocarbon radial having one or more double bonds and containing a number of carbon atoms as given.

The term "alkanoyl", alone or in combination, means an acyl radical derived from an alkanecarboxylic acid wherein alkane means a radical as defined above for alkyl. Examples of alkanoyl radicals include acetyl, propionyl, butyryl, valeryl, 4-methylvaleryl, and the like.

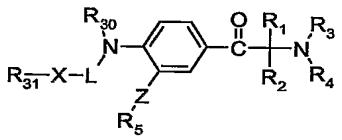
The term "alkenoyl", alone or in combination, means an acyl radical derived from an alkenecarboxylic acid wherein alkene means a radical as defined above for alkenyl.

The term "alkadiene" alone or in combination includes compounds with at least two carbon to carbon double bonds and containing a number of carbon atoms as given.

All these compounds have at least one basic amino group and can therefore be converted into the corresponding salts by addition of acids. The acids can be inorganic or organic acids. Examples of such acids are HCl, HBr, H_2SO_4, H_3PO_4, mono- or polycarboxylic acids, for example, acetic acid, oleic acid, succinic acid, sebacic acid, tartaric acid or CF_3COOH, and sulfonic acids, for example, CH_3SO_3H.

Preferred photoinitiators:

A compound of the formula I or II



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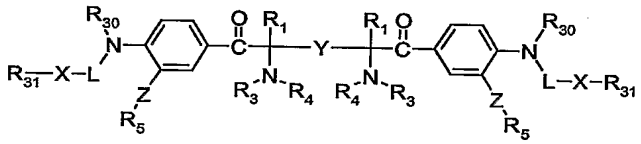


II

wherein

L is a linker;

X is –O-, -S- or $–NR_{32}$-

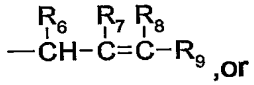
Y is C_1-C_8-alkylene;

Z is a direct bond;

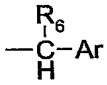
R_1 and R_2 are independently of each other either

(a) linear or branched C_1-C_{12}-alkyl;

(b) a radical of the formula;



(c) a radical of the formula



wherein Ar is phenyl, which is unsubstituted or substituted by one or more of the groups NO_2, $-N(R_{10})_2$, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylthio, phenoxy;

R_3 is C_1-C_4-alkyl, C_2-C_4-alkyl substituted by hydroxy, C_1-C_4-alkoxy; C_3-C_5-alkenyl;

R_4 independently of R_3 has one of the meanings of R_3; or R_4 together with R_3 is C_4-C_5-alkylene that may be interrupted by -O-, $-N(R_{13})$-;

R_5 is hydrogen;

R_6, R_7, R_8 and R_9 independently of each other are hydrogen or methyl;

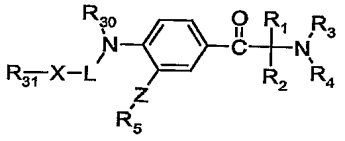
R_{10} is hydrogen, C_1-C_4-alkyl or C_3-C_5-alkenyl;

R_{13} is hydrogen or C_1-C_4-alkyl;

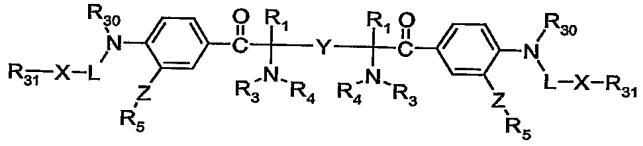
R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl); allyl, cyclohexyl or C_7-C_9-phenylalkyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl; or -CO-NH-C_1-C_{12}-alkyl or –CO-NH-(C_0-C_{12}-alkylen)-N=C=O, optionally interrupted by one or two phenylene,methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-Isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl;

R_{32} is hydrogen or C_1-C_{12}-alkyl.

Especially preferred are compounds of the formula I or II



I



II

wherein

L is linear or branched C_2-C_{18}-alkanediyl;

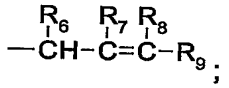
X is –O-; Y is C_1-C_6-alkylene;

Z is a direct bond;

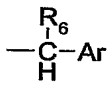
R_1 and R_2 are independently of each other either

(a) linear or branched C_1-C_3-alkyl;

(b) a radical of the formula;



(c) a radical of the formula



where Ar is phenyl, which is unsubstituted or substituted by CH_3-NO_2 or -$N(R_{10})_2$;

R_3 is methyl,

R_4 is methyl or R_4 together with R_3 is C_5-alkylene that is interrupted by -O-;

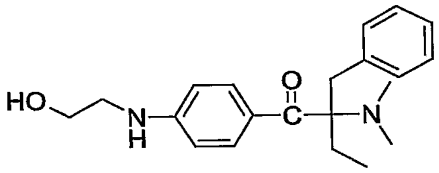
R_5 is hydrogen;

R_6, R_7, R_8 and R_9 are hydrogen;

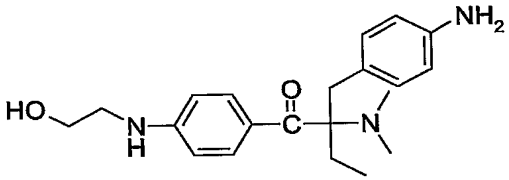
R_{10} is hydrogen;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy; C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or C_3-C_5-alkenoyl.

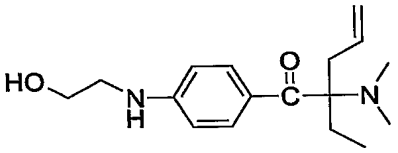
Examples



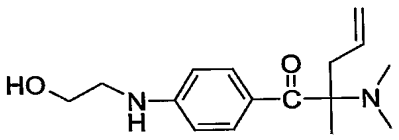
2-benzyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-butanone



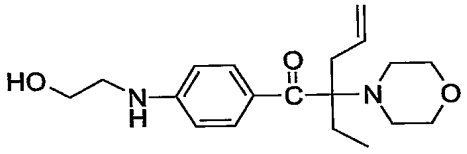
2-[(4-aminophenyl)methyl]-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-butanone



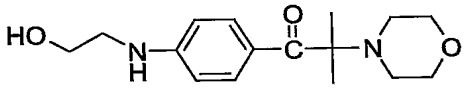
2-ethyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-pent-4-en-1-one



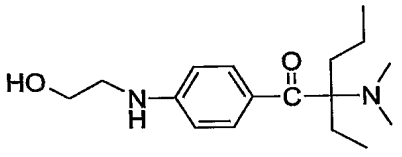
1-[4-(2-hydroxyethylamino)phenyl]-2-methyl-2-dimethylamino-1-pent-4-en-1-one



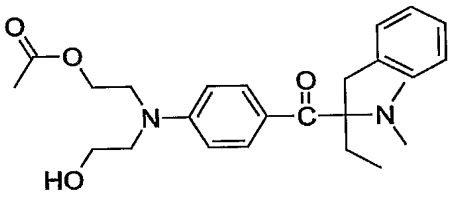
2-ethyl-1-[4-(2-hydroxyethylamino)phenyl]-2-(morpholin-4-yl)-1-pent-4-en-1-one



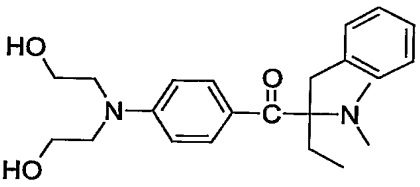
1-[4-(2-hydroxyethylamino)phenyl]-2-methyl-2-(morpholin-4-yl)-1-propanone



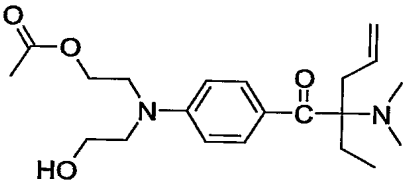
2-ethyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-pentan-1-one



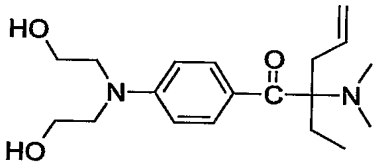
2-benzyl-2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-1-butanone



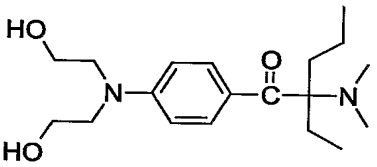
2-benzyl-1-{[4-[bis(2-hydroxyethy)amino]phenyl}-2-dimethylamino-1-butanone



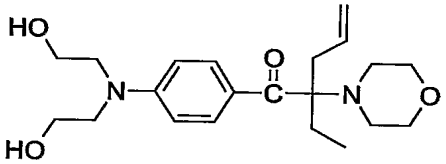
2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-2-ethyl-1-pent-4-en-1-one



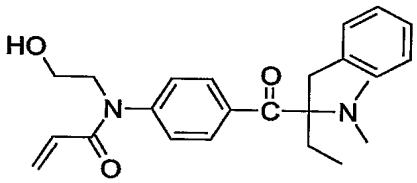
2-dimethylamino-1-{[4-[bis(2-hydroxyethy)amino]-phenyl}-2-ethyl-1-pent-4-en-1-one



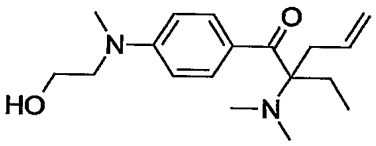
2-dimethylamino-1-{[4-[bis(2-hydroxyethy)amino]-phenyl}-2-ethyl-1-pentan-1-one



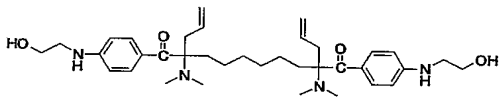
1-{[4-[bis(2-hydroxyethyl)amino]-phenyl}-2-ethyl-2-morpholin-4-yl)-1-pent-4-en-1-one



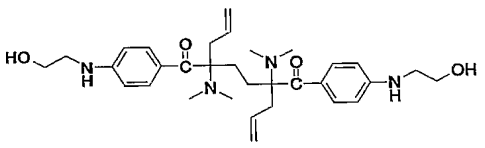
2-benzyl-1-{4-[(2-hydroxyethyl)-acryloyl-amino]phenyl}-2-dimethylamino-1-butanone



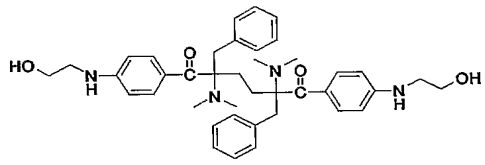
2-dimethylamino-2-ethyl-1-{4-[(2-hydroxy-ethyl)-methyl-amino]-phenyl}-pent-4-en-1-one



2,8-diallyl-2,8-bis-dimethylamino-1.9-bis-[4-(2-hydroxy-ethylamino)-phenyl]-nonane-1,9-dione



2,5-diallyl-2,5-bis-dimethylamino-1.6-bis-[4-(2-hydroxy-ethylamino)-phenyl]-hexan-1,6-dione

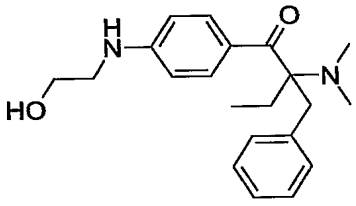


2,5-dibenzyl-2,5-bis-dimethylamino-1.6-bis-[4-(2-hydroxy-ethylamino)-phenyl]-hexan-1,6-dione

Preparation of the novel photoinitiators:

The compounds of formula I can be prepared starting from known ketones by C-alkylation or C-benzylation. The amino group $-NR_3R_4$ is preferably introduced before the alkylation or benzylation. The synthesis is carried out in the sequence of reaction steps as described in EP0 284561B1 or US5077402.

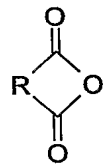
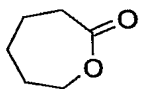
For example, a halogeno aryl ketone such as e.g. 4-fluorobutyrophenone can be used as starting ketone. After bromination the dimethylamino group is introduced followed by a benzylation reaction. The halogen is then replaced by ethanolamine in a nucleophilic replacement reaction. The following key compound is obtained.



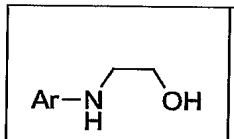
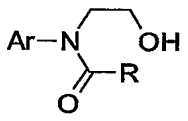
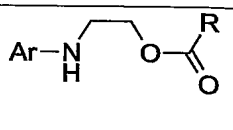
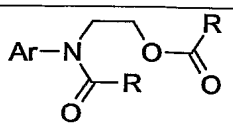
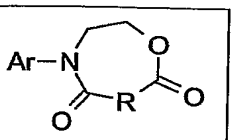
The above key compound (Ex. 1, named Educt E) or the compounds according to Examples 2-18 can be further reacted with reagents such as those listed below. The radical R in the following lists may carry 1-n of the functional groups indicated. If n > 1, the polyfunctional reagent may be reacted with 1-n equivalents of the educt (e.g. E).

Reagents with which E can be reacted are:

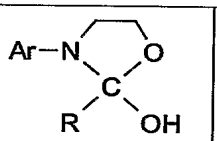
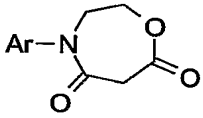
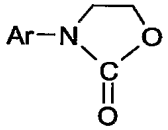
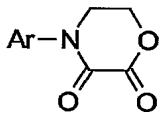
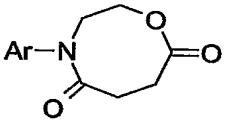
1) acids, acid halides, linear or branched acid anhydrides, $COCl_2$ or lactones

Educt E and R-COOH, R-COCl, R-CO-O-CO-R,  or 

Amides (A), esters (B) or amide-ester compounds (AB), (ABR) are obtained.

				
E	A	B	AB	ABR

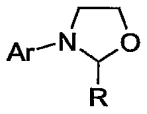
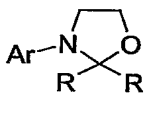
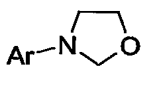
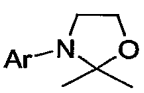
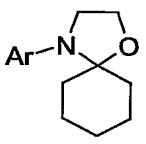
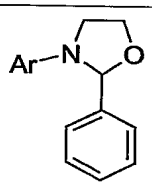
Examples of cyclic amide-ester compounds (ABR) are:

				
intermediate	7-ring	5-ring	6-ring	8-ring

2) Reaction with aldehydes or ketones

Educt E and R-CHO, R-CO-R

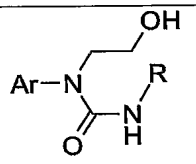
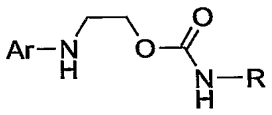
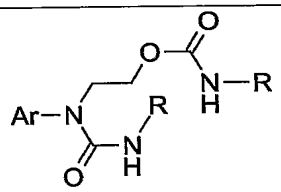
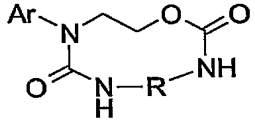
2-Oxazolidine compounds (A) or 2-oxazolidine compounds (B) and further cyclic products are obtained.

					
A	B				

3) Reaction with isocyanates

Educt E and R-N=C=O

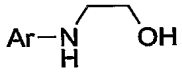
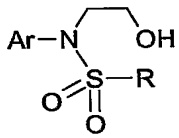
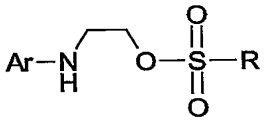
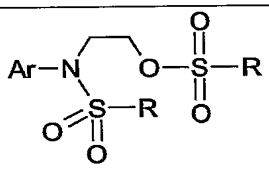
Urea derivatives (A) or urethane derivatives (B) or urea-urethane derivatives (AB) or cyclic urea-urethane derivatives (ABR) are obtained.

			
A	B	AB	ABR

4) Reaction with sulfonic acid chloride.

Educt E and R-SO_2-Cl

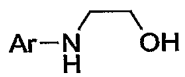
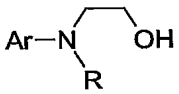
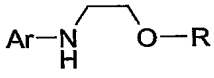
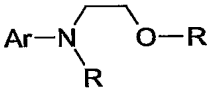
Sulfonamide derivatives (A), sulfonic acid esters (B) or sulfonamide-sulfonic acid derivatives (AB) are obtained.

			
E	A	B	AB

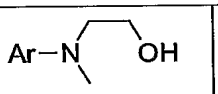
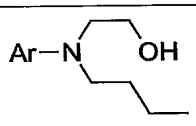
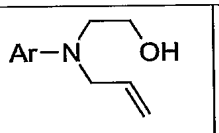
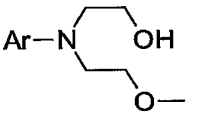
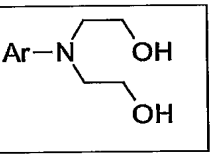
5) Alkylation, reaction with R-X

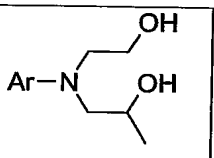
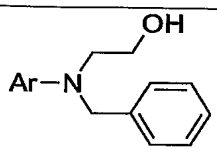
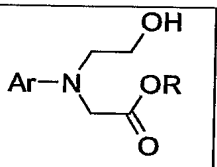
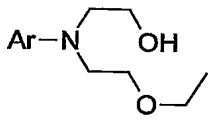
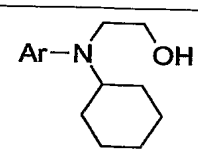
Educt E and R-halogen or R-O-SO_2-R' or other known alkylations agents,

Amines (A), ethers (B) or amine-ether derivatives (AB) are obtained.

			
E	A	B	AB

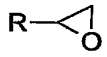
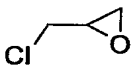
Examples are:

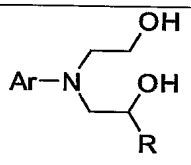
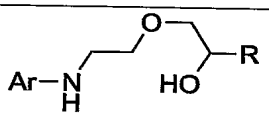
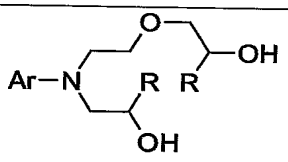
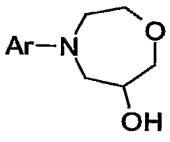
				

The compounds thus obtained can in turn be used as starting materials E' for as described under 1), 2), 3), 4), 6), 7) or 8)

6) Reaction with epoxides or epichlorhydrine

Educt E and  or 

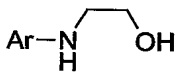
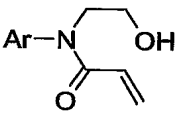
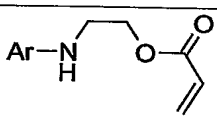
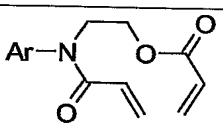
Hydroxyalkylamine compounds (A) or hydroxyalkylether compounds (B) or hydroxyalkylamine-hydroxyalkylether-compounds (AB) or cyclic hydroxyalkylamine-hydroxyalkylether-compounds (ABR) are obtained.

			
A	B	AB	ABR

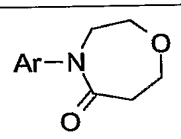
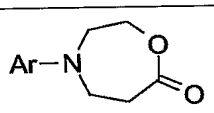
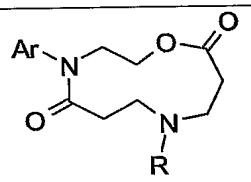
7) Reaction with acrylates or methacrylates

Educt E and CH_2=CH-CO-OH or CH_2=C(CH_3)-CO-OH or with the corresponding acid chlorides.

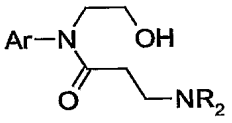
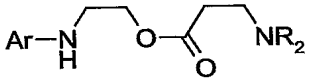
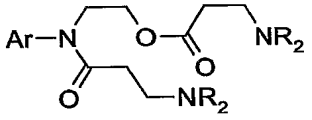
Acrylamides (A) or acrylester (B) or amide-ester-compounds (AB) are obtained.

			
E	A	B	AB

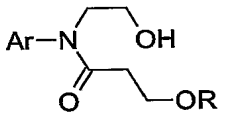
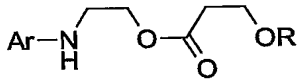
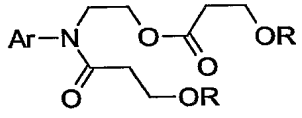
Examples for cyclic compounds obtained from the above compounds by intramolecular Michael addition reaction.

		
A'	B'	A'B'

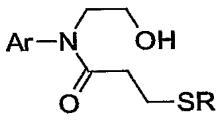
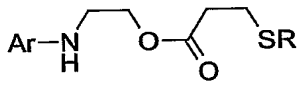
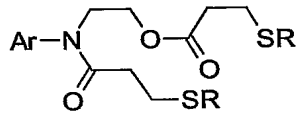
7a) The acrylamides (A), acrylester (B) or amide-ester compounds (AB) can be reacted with amines to obtain

		
A'	B'	A'B'

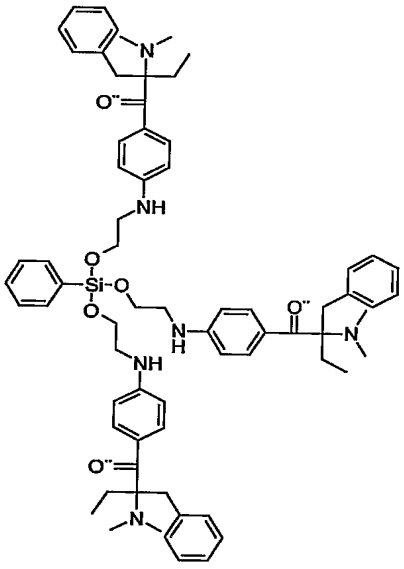
7b) The acrylamides (A), acrylester (B) or amide-ester compounds (AB) can be reacted with alcohols to obtain

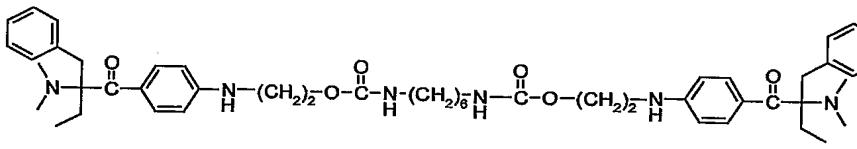
		
A'	B'	A'B'

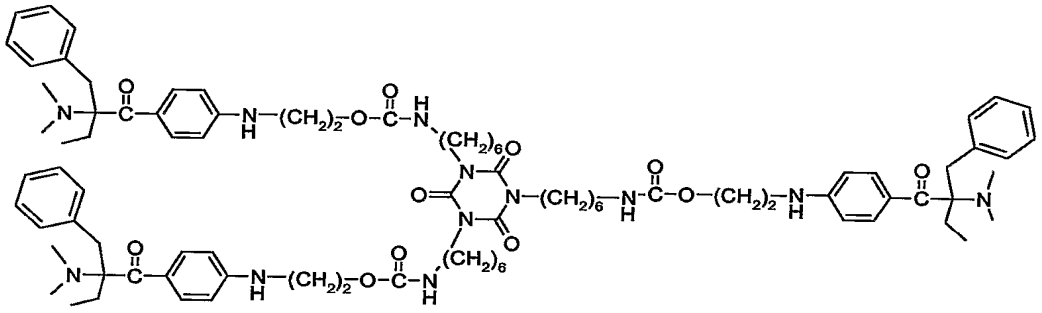
7c) The acrylamides (A), acrylester (B) or amide-ester compounds (AB) can be reacted with thioalcohols to obtain

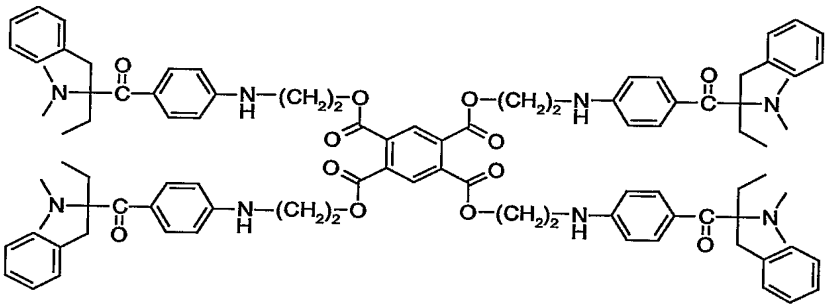
		
A'	B'	A'B'

Examples of multifunctional photoinitiators are:







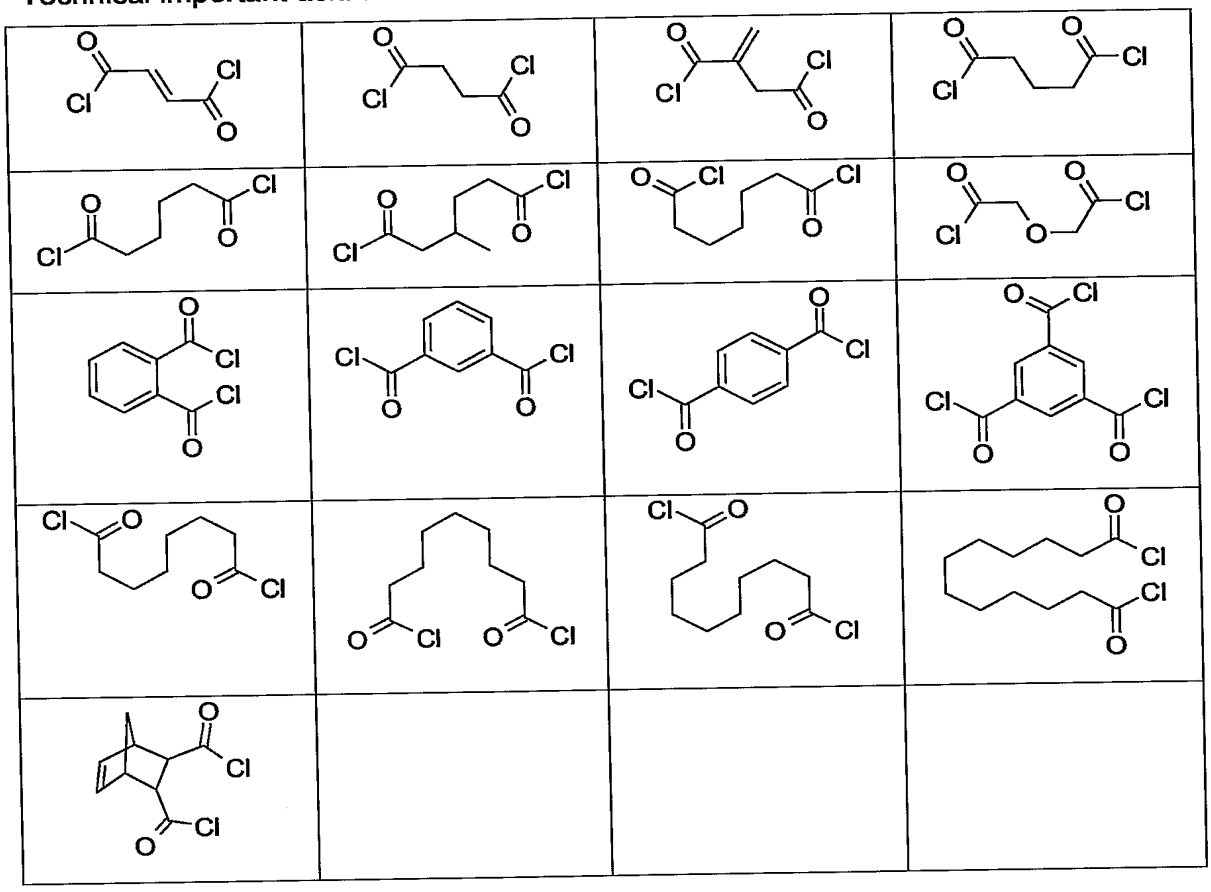


5

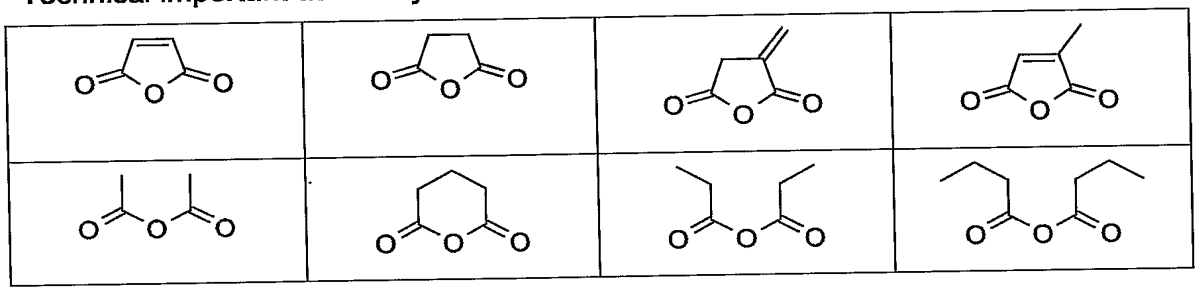
Dimeric or oligomeric products:

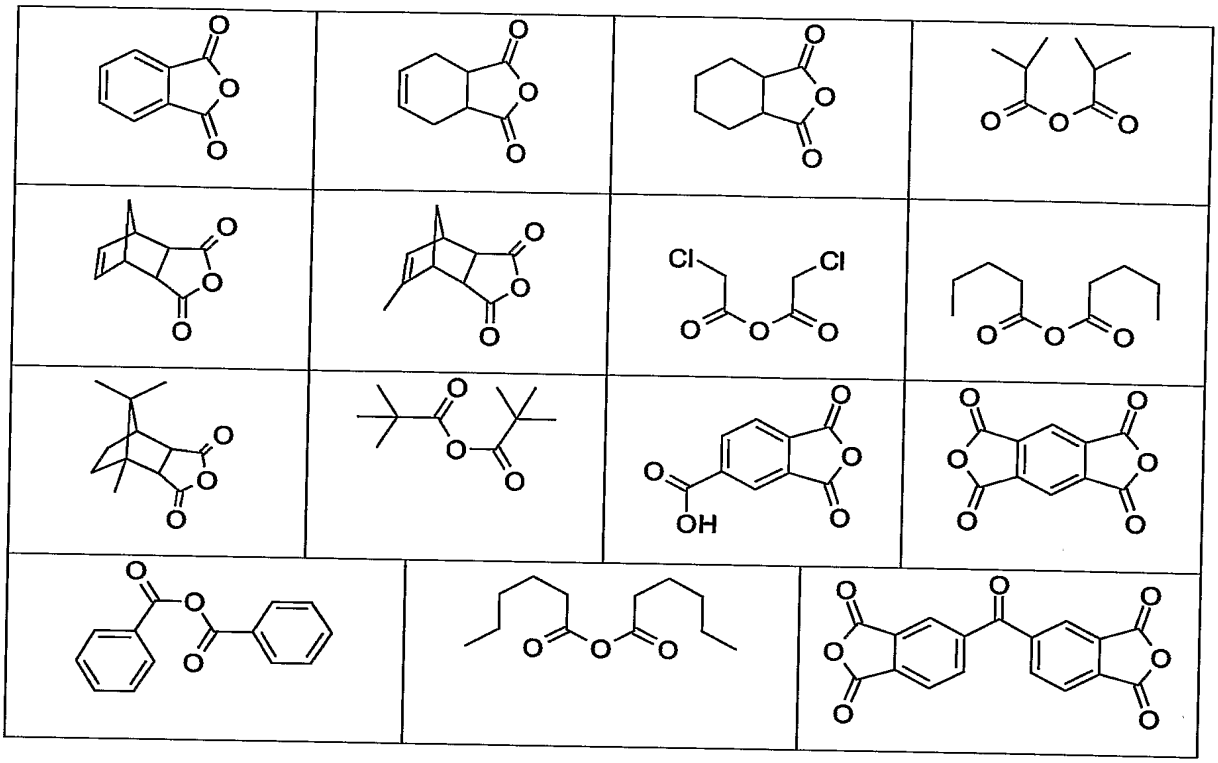
The compoundsof Examples 1-18 may be reacted with following acid halides, acid anhydrides, di-or poly carboxylic acids, di-or polyaldehydes, di- or oligoisocyanates, di-or oligoepoxides, di-or polyamines, di-or oligoalcohols, di-or polythiols to obtain di-or oligomeric product.

Technical important acid chlorides:

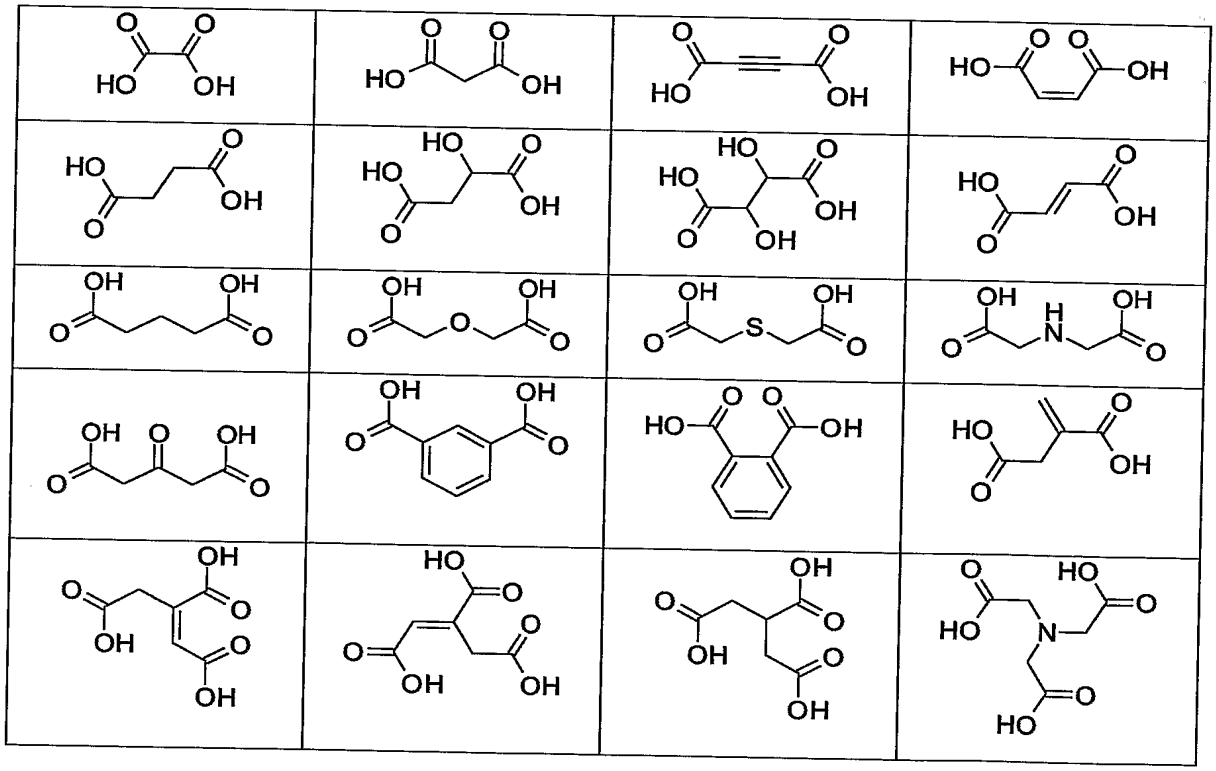


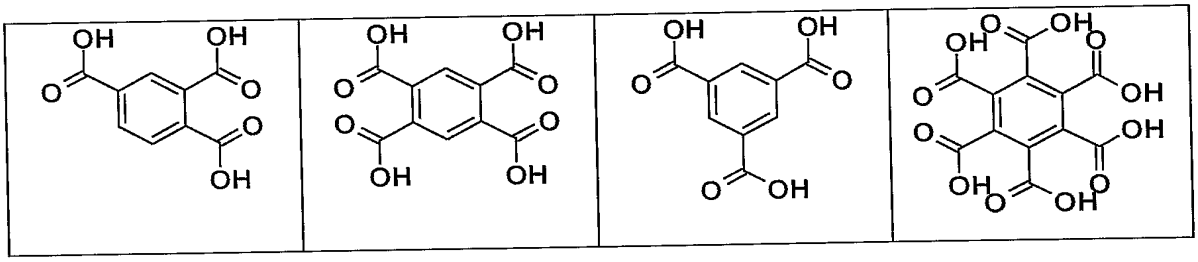
Technical important acid anhydrides:

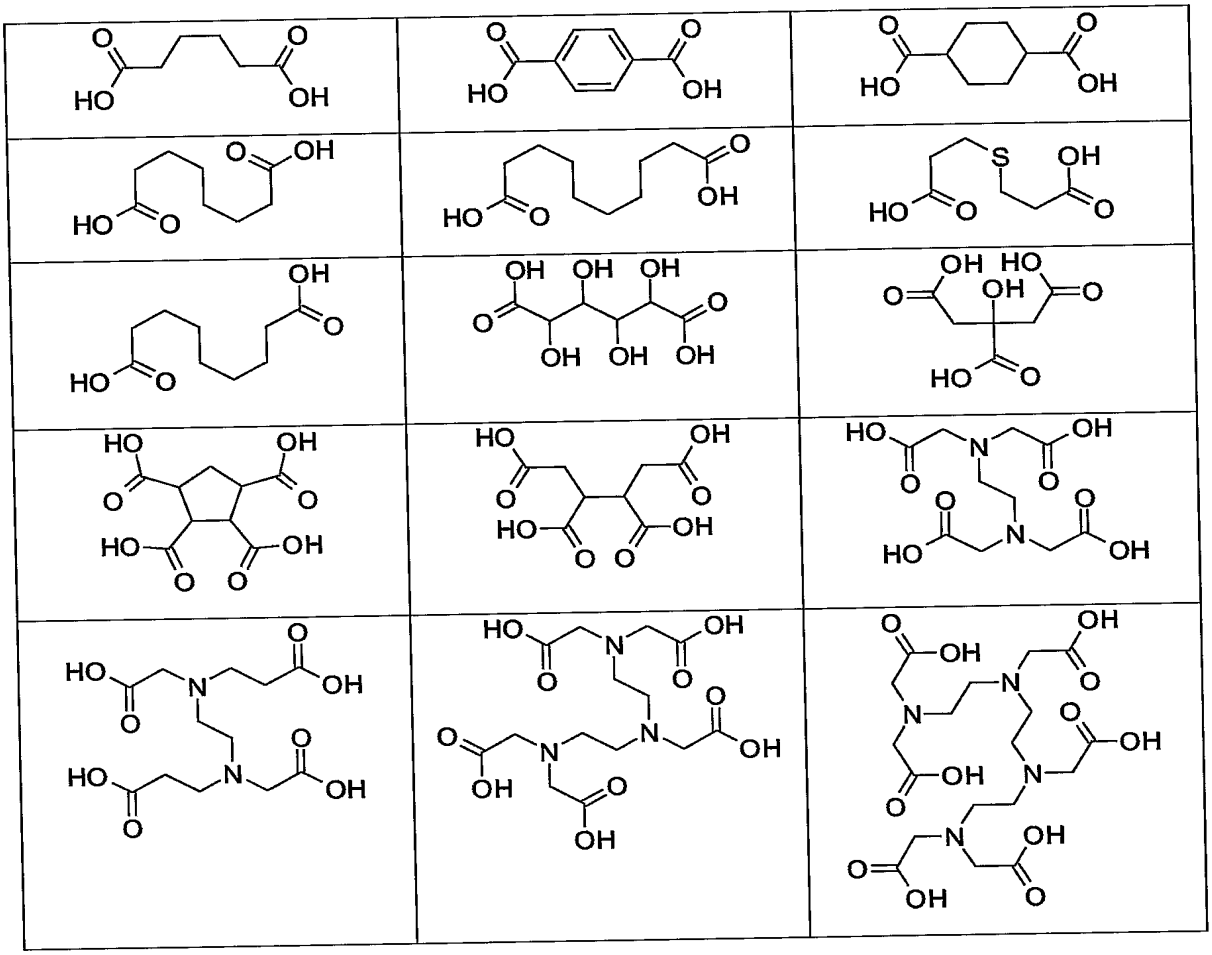




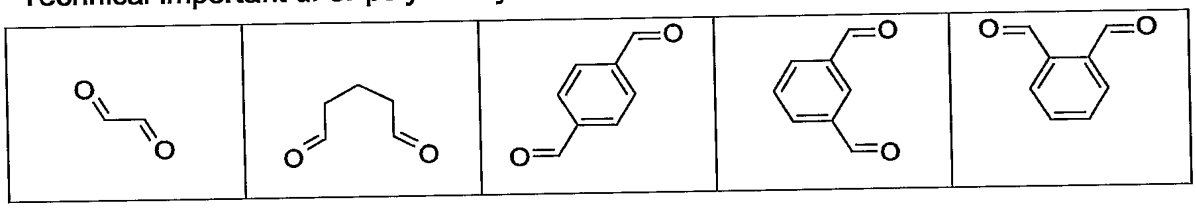
Technical important di-or polycarboxylic acids





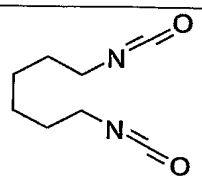
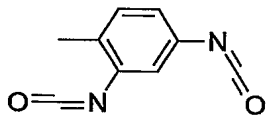
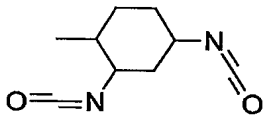
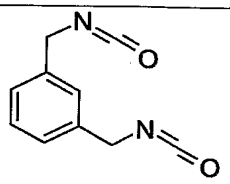
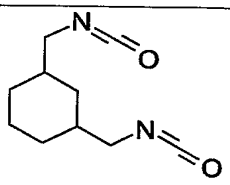
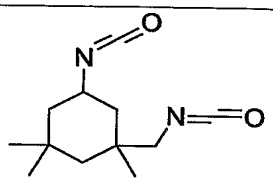
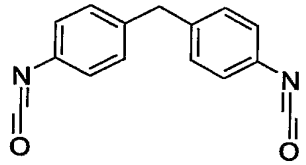
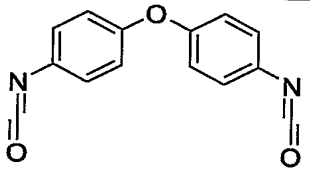
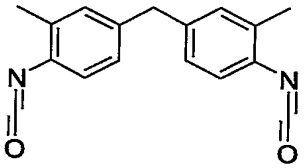
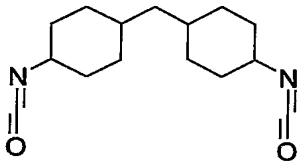
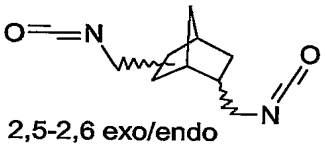
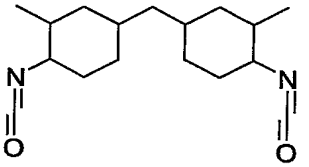
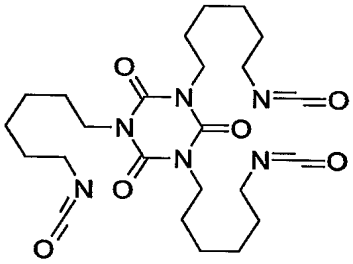
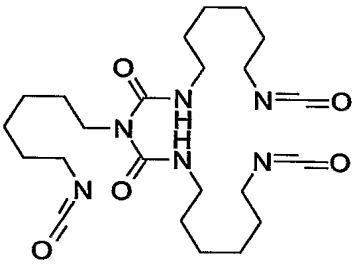
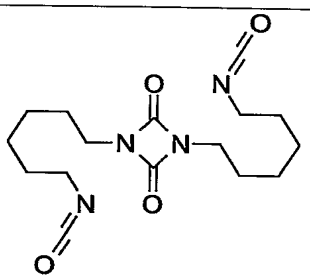
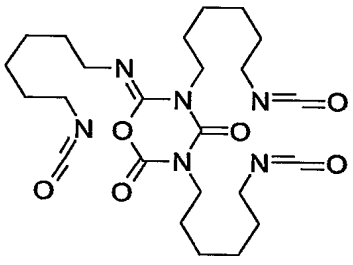
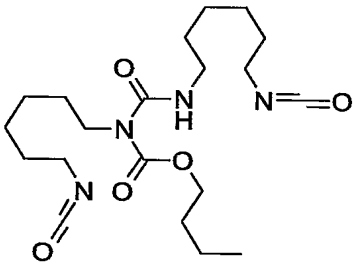
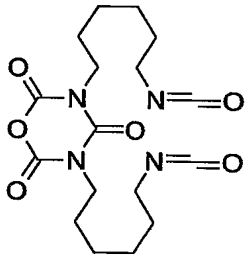
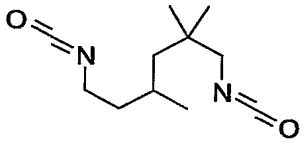


Technical important di-or polyaldehydes



5

Technical important di-or polyisocyanates

		
		
		
	 2,5-2,6 exo/endo	
		
		
		

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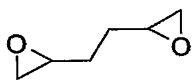	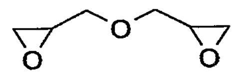	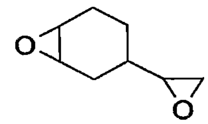
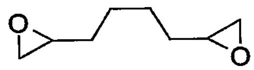	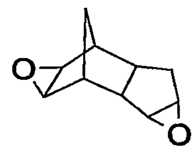	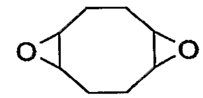
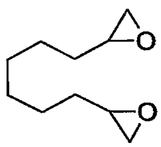	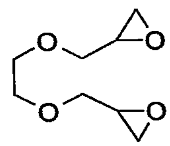	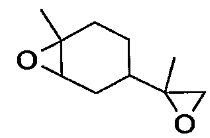
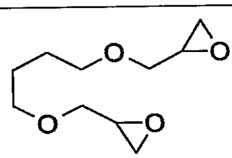	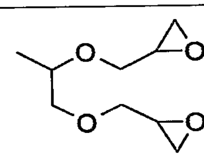	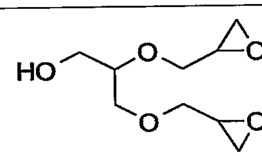
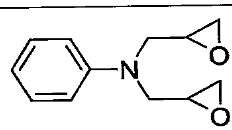	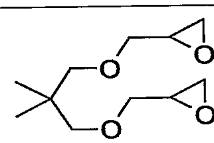	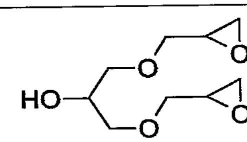
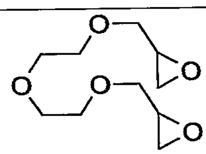	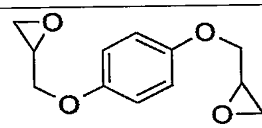	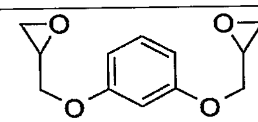
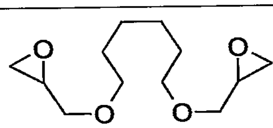	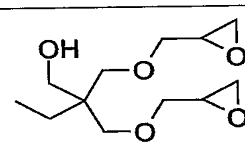	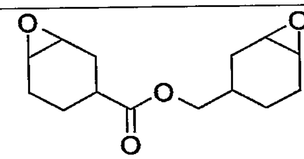
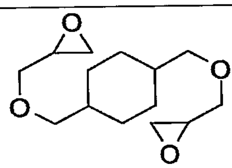	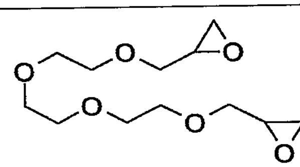	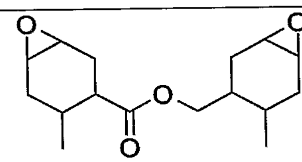

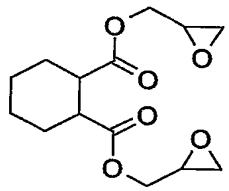	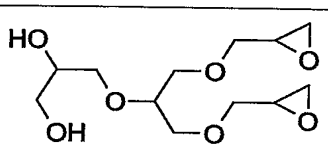	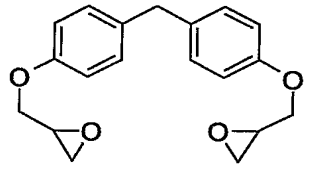
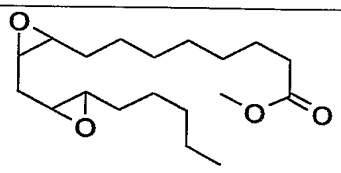	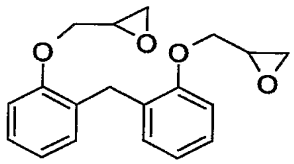	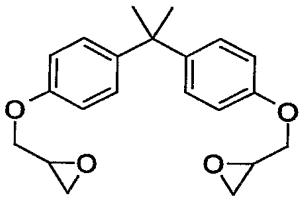
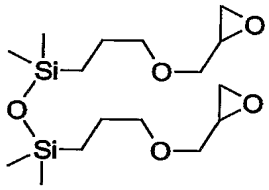	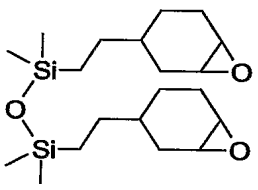	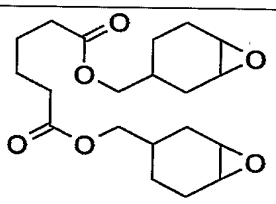
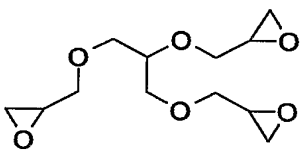	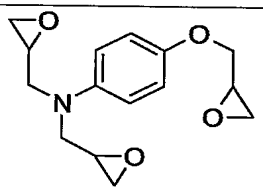	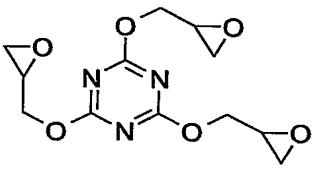
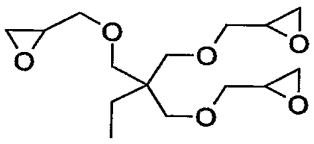		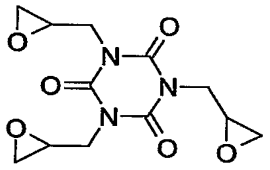
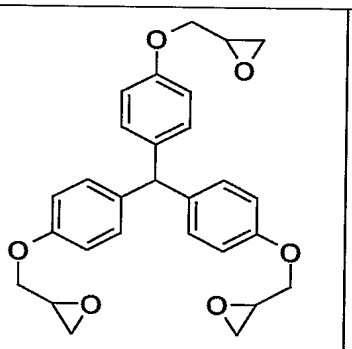	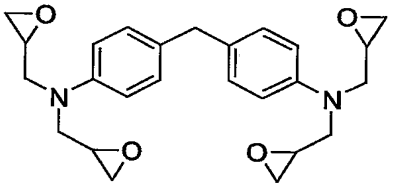	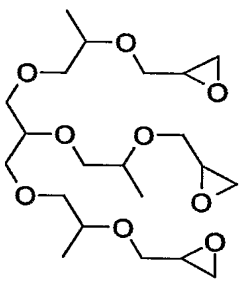

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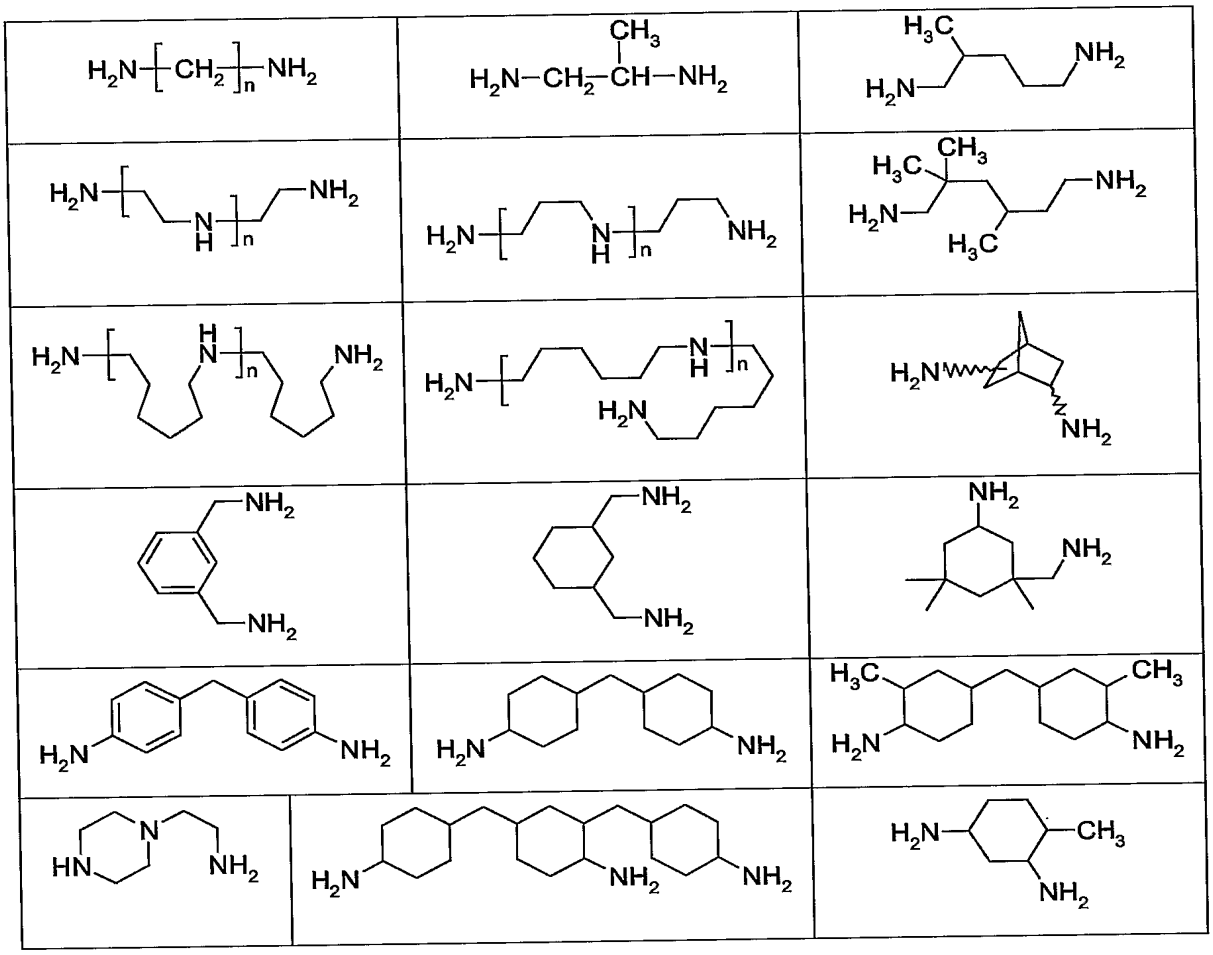

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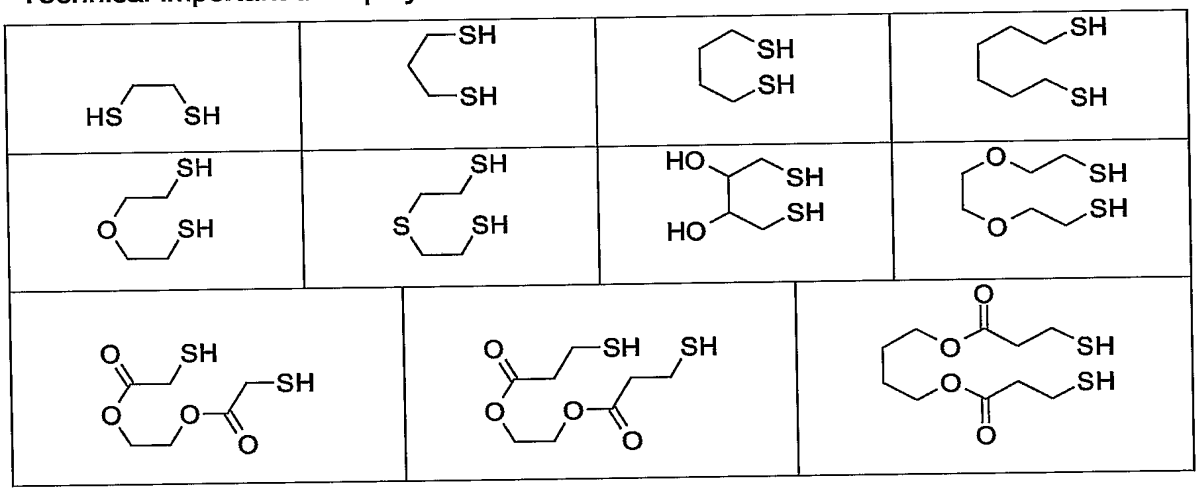
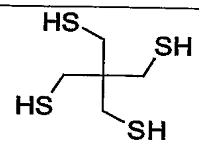
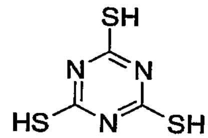
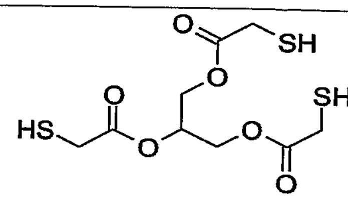
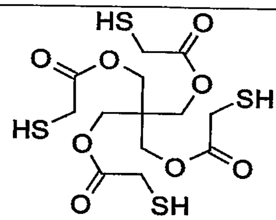
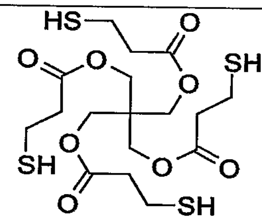
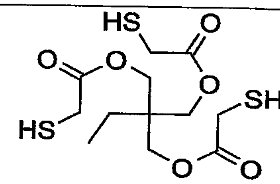
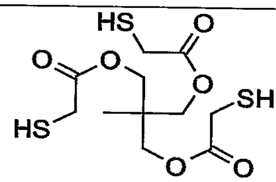
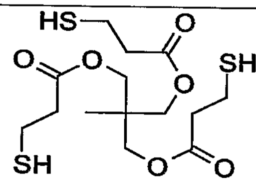
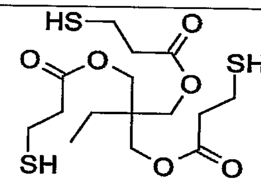
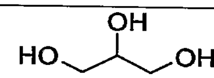
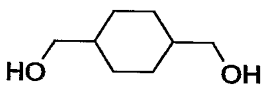
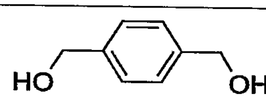
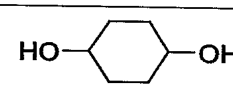
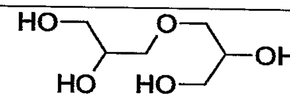
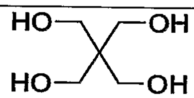
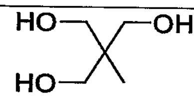
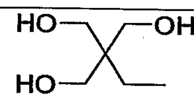
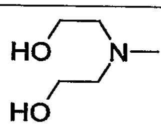
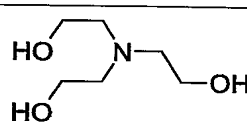
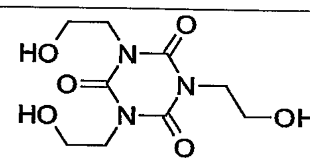
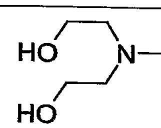
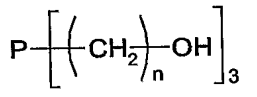
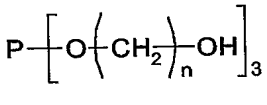
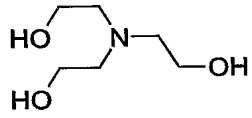
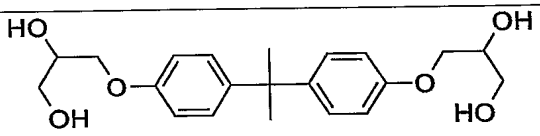
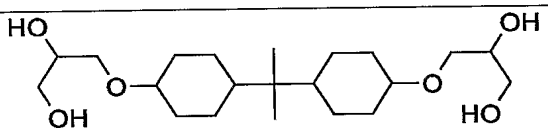
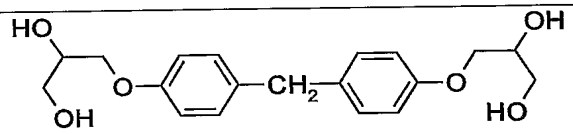
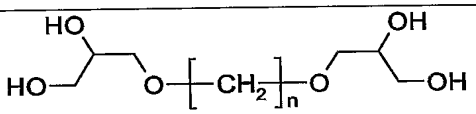
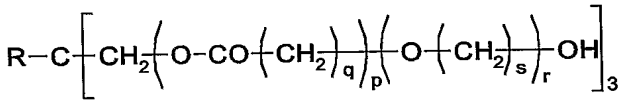
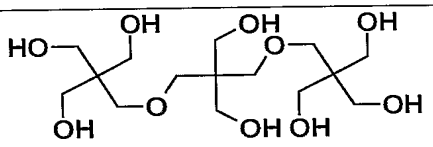


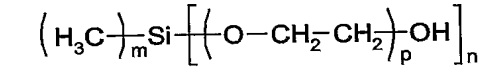
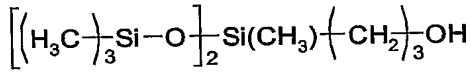
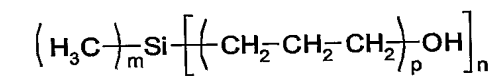
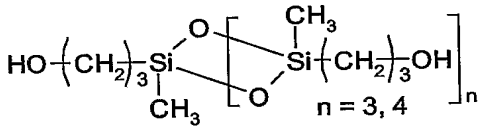
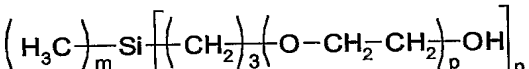
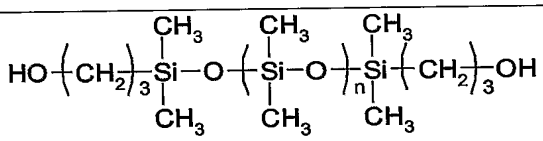
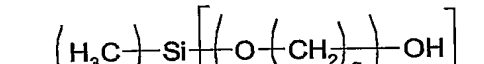
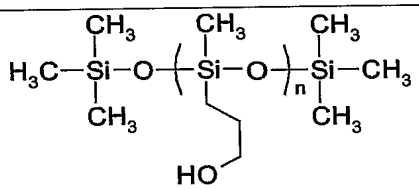
Technical important di-or polyalcohols:

$HO-[CH_2]_n-OH$	$HO-[CH_2-CH(CH_3)]_n-OH$	
		
$HO-[CH_2-CH_2-O]_n-H$	$HO-[CH_2-CH(CH_3)-O]_n-H$	
		
		
$O{=}P-[(CH_2)_n-OH]_3$	$O{=}P-[O-(CH_2)_n-OH]_3$	

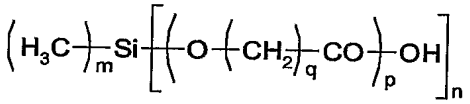
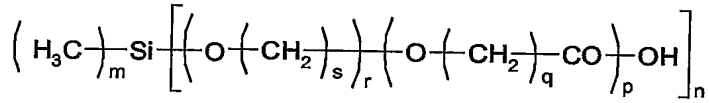
	
	
 R = C_1-C_3-Alkyl q = 3 - 5 p = 1 - 6 s = 2 - 6 r = 1 - 6	

Si-containing di-and oligoalcohols.

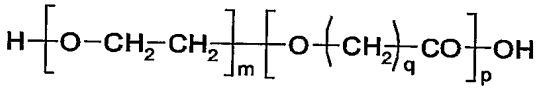
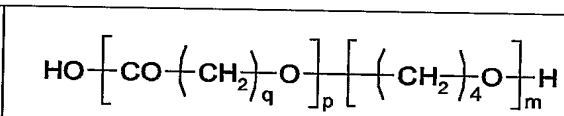
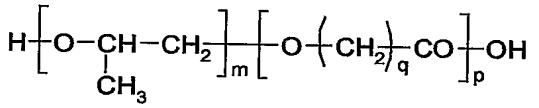
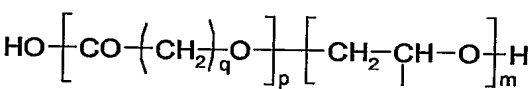
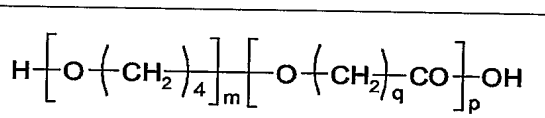
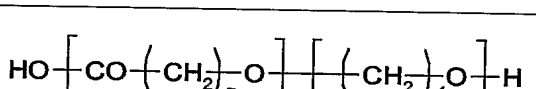
 n > 0 n + m = 4 p = 1 - 6	
 n > 0 n + m = 4 p = 1 - 2	 n = 3, 4
 n > 0 n + m = 4 p = 1 - 4	
 n > 0 n + m = 4 q = 2 - 6 p = 0 - 6	

5

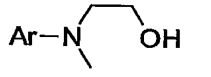
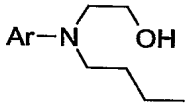
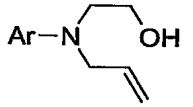
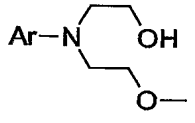
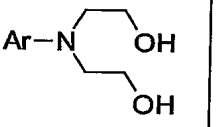
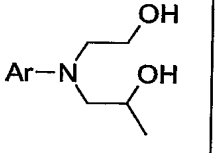
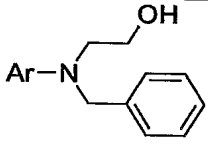
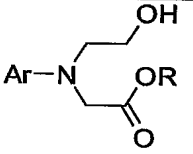
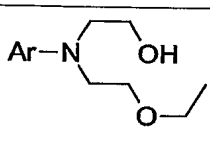
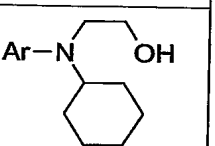
Si-containing di- and oligo-lactone-derivates

 n > 0 n + m = 4 q = 3 - 5 p = 1 - 6
 n > 0 n + m = 4 s = 2 - 6 r = 1 - 6 q = 3 - 5 p = 1 - 6

Linking moieties between initiator and Si

 m = 1 - 6 q = 3 - 5 p = 1 - 6	 q = 3 - 5 p = 1 - 6 m = 1 - 6
 m = 1 - 6 q = 3 - 5 p = 1 - 6	 q = 3 - 5 p = 1 - 6 m = 1 - 6
 m = 1 - 6 q = 3 - 5 p = 1 - 6	 q = 3 - 5 p = 1 - 6 m = 1 - 6

Examples for the alkylation at the N-atom are:

According to the invention, the compounds of the formula I, II can be used as photoinitiators for photopolymerization of ethylenically unsaturated compounds or mixtures containing such compounds.

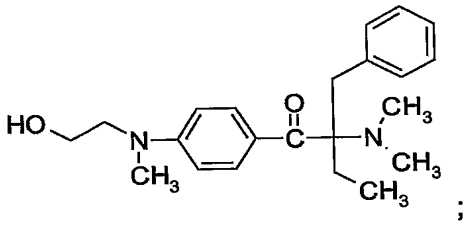
Thus, the invention relates also to a composition comprising

(A) at least one ethylenically unsaturated compound,

(B) a photoinitiator of formula I and/or II;

(C) optionally further binders or additives,

(D) optionally further photoinitiators or co-initiators, with the proviso that the following compounds are excluded: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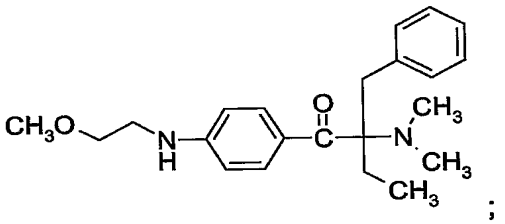
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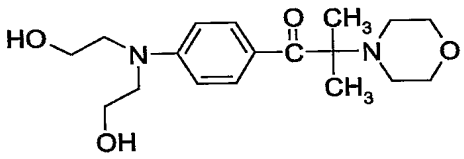
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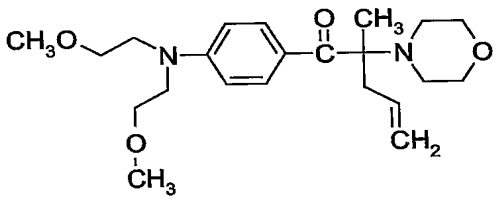

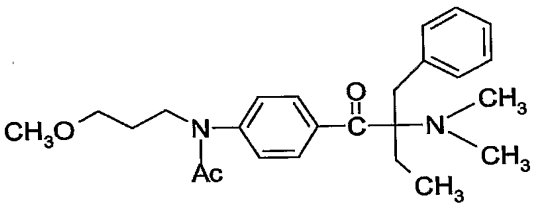
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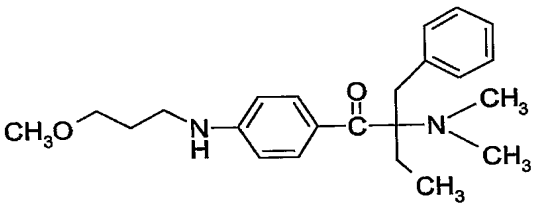

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Suitable ethylenically unsaturated compounds (A)

The unsaturated compounds (A) may contain one or more olefinic double bonds. They may be low molecular weight (monomeric) or higher molecular weight (oligomeric).

Examples of monomers having one double bond include alkyl and hydroxyalkyl acrylates and methacrylates, for example methyl, ethyl, butyl, 2-ethylhexyl and 2-hydroxyethyl acrylate, isobornyl acrylate, methyl methacrylate and ethyl methacrylate. Further examples are acrylonitrile, acrylamide, methacrylamide, N-substituted (meth)acrylamides, vinyl esters, such as vinyl acetate, vinyl ethers, such as isobutyl vinyl ether, styrene, alkyl- and halo-styrenes, N-vinylpyrrolidone, vinyl chloride and vinylidene chloride.

Examples of monomers having a plurality of double bonds include ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, hexamethylene glycol diacrylate and bisphenol-A diacrylate, 4,4'-bis(2-acryloyloxyethoxy)diphenylpropane, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, vinyl acrylate, divinylbenzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate and tris(2-acryloylethyl) isocyanurate.

Examples of higher molecular weight (oligomeric) polyunsaturated compounds include acrylated epoxy resins, acrylated or vinyl ether or epoxy group-containing polyesters, polyurethanes and polyethers.

Further examples of unsaturated oligomers include unsaturated polyester resins, which are usually prepared from maleic acid, phthalic acid and one or more diols and have molecular weights of about from 500 to 3000. In addition, it is also possible to use vinyl ether monomers and oligomers, and also maleate-terminated oligomers having polyester, polyurethane, polyether, polyvinyl ether and epoxide main chains. Combinations of vinyl ether group-carrying oligomers and polymers, as described in WO 90/01512, are especially suitable, but copolymers of monomers functionalized with maleic acid and vinyl ether also come into consideration.

Also suitable are compounds having one or more free-radical-polymerizable double bonds. Preferably, the free-radical-polymerizable double bonds in such compounds are in the form of (meth)acryloyl groups. (Meth)acryloyl and (meth)acryl, here and in the following, denote acryloyl and/or methacryloyl, and acryl and/or methacryl, respectively. Preferably at least two polymerizable double bonds in the form of (meth)acryloyl groups are present in the molecule. The compounds may be, for example, (meth)acryloyl-functional oligomeric and/or polymeric

compounds of poly(meth)acrylate. The number average molecular weight of such a compound may be, for example, from 300 to 10 000, preferably from 800 to 10 000. The compounds containing preferably free-radical-polymerizable double bonds in the form of (meth)acryloyl groups can be obtained according to customary methods, for example by reaction of poly(meth)acrylates with (meth)acrylic acid. That method, and further methods of preparation, are described in the literature and are known to the person skilled in the art. Such unsaturated oligomers can also be termed prepolymers.

Functional polymers:

As component (A) it is also possible to use unsaturated acrylates having reactive functional groups. The reactive functional group can, e.g., be selected from hydroxyl, thiol, isocyanate, epoxy, anhydride, carboxyl, amino and blocked amino groups. Examples of OH-group-containing unsaturated acrylates are hydroxyethyl acrylates, hydroxybutyl acrylates and also glycidyl acrylates.

Examples of suitable monomers normally used to form the backbone (the base polymer) of such functionalized acrylate and methacrylate polymers include, for example, acrylate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate etc.. In addition, suitable amounts of functional monomers are co-polymerized during the polymerization in order to obtain the functional polymers in that manner. Acid-functionalized acrylate or methacrylate polymers are obtained using acid-functional monomers, such as acrylic acid and methacrylic acid. Hydroxy-functional acrylate or methacrylate polymers are obtained from hydroxy-functional monomers, such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 3,4-dihydroxybutyl methacrylate, or from acrylates derived from glycerol derivatives.

Epoxy-functionalized acrylate or methacrylate polymers are obtained using epoxy-functional monomers, such as glycidyl methacrylate, 2,3-epoxybutyl methacrylate, 3,4-epoxybutyl methacrylate, 2,3-epoxycyclohexyl methacrylate, 10,11-epoxyundecyl methacrylate etc..

Similarly, it is possible, for example, for isocyanate-functionalized polymers to be prepared from isocyanate-functionalized monomers, for example meta-isopropenyl-α,α-dimethylbenzyl isocyanate. Amino-functionalized polymers include, for example, polyacrylamides. Nitrile-group-containing polymers include, for example, polyacrylonitriles.

Esters

There are especially suitable, for example, esters of ethylenically unsaturated mono- or poly-functional carboxylic acids and polyols or polyepoxides, and polymers having ethylenically unsaturated groups in the chain or in side groups, e.g. unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, alkyd resins, polybutadiene and butadiene copolymers, polyisoprene and isoprene copolymers, polymers and copolymers having (meth)acryl groups in side chains, and also mixtures of one or more such polymers.

Examples of suitable mono- or poly-functional unsaturated carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, maleic acid, fumaric acid, itaconic acid, and unsaturated fatty acids such as linolenic acid or oleic acid. Acrylic acid and methacrylic acid are preferred.

It is also possible, however, for saturated di- or poly-carboxylic acids to be used in admixture with unsaturated carboxylic acids. Examples of suitable saturated di- or poly-carboxylic acids include, for example, tetrachlorophthalic acid, tetrabromophthalic acid, phthalic anhydride, adipic acid, tetrahydrophthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, heptanedicarboxylic acid, sebacic acid, dodecanedicarboxylic acid, hexahydrophthalic acid etc..

Suitable polyols are aromatic and especially aliphatic and cycloaliphatic polyols. Examples of aromatic polyols include hydroquinone, 4,4'-dihydroxydiphenyl, 2,2-di(4-hydroxyphenyl)-propane, and novolaks and resols. Examples of polyepoxides are those based on the said polyols, especially the aromatic polyols, and epichlorohydrin. Also suitable as polyols are polymers and copolymers that contain hydroxyl groups in the polymer chain or in side groups, e.g. polyvinyl alcohol and copolymers thereof and polymethacrylic acid hydroxyalkyl esters or copolymers thereof. Further suitable polyols are oligoesters having hydroxyl terminal groups.

Examples of aliphatic and cycloaliphatic polyols include alkylenediols having preferably from 2 to 12 carbon atoms, such as ethylene glycol, 1,2- and 1,3-propanediol, 1,2-, 1,3- and 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of preferably from 200 to 1500, 1,3-cyclopentanediol, 1,2-, 1,3- and 1,4-cyclohexanediol, 1,4-dihydroxymethylcyclohexane,

glycerol, tris(β-hydroxyethyl)amine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol.

The polyols may be partially or fully esterified with one or with different unsaturated carboxylic acid(s), it being possible for the free hydroxyl groups in partial esters to be modified, for example etherified, or esterified with other carboxylic acids.

Examples of esters are:
trimethylolpropane triacrylate, trimethylolethane triacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tripentaerythritol octaacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol tetramethacrylate, tripentaerythritol octamethacrylate, pentaerythritol diitaconate, dipentaerythritol trisitaconate, dipentaerythritol pentaitaconate, dipentaerythritol hexaitaconate, ethylene glycol diacrylate, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol diitaconate, sorbitol triacrylate, sorbitol tetraacrylate, pentaerythritol-modified triacrylate, sorbitol tetramethacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, oligoester acrylates and methacrylates, glycerol di- and tri-acrylate, 1,4-cyclohexane diacrylate, bisacrylates and bismethacrylates of polyethylene glycol having a molecular weight of from 200 to 1500, and mixtures thereof. The following esters are also suitable: dipropylene glycol diacrylate, tripropylene glycol diacrylate, 1,6-hexanediol diacrylate, glycerol ethoxylate triacrylate, glycerol propoxylate triacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, pentaerythritol ethoxylate tetraacrylate, pentaerythritol propoxylate triacrylate, pentaerythritol propoxylate tetraacrylate, neopentyl glycol ethoxylate diacrylate, neopentyl glycol propoxylate diacrylate.

Amides

Also suitable as component (A) are the amides of identical or different unsaturated carboxylic acids and aromatic, cycloaliphatic and aliphatic polyamines having preferably from 2 to 6, especially from 2 to 4, amino groups. Examples of such polyamines are ethylenediamine, 1,2- and 1,3-propylenediamine, 1,2-, 1,3- and 1,4-butylenediamine, 1,5-pentylenediamine,

1,6-hexylenediamine, octylenediamine, dodecylenediamine, 1,4-diaminocyclohexane, isophorone diamine, phenylenediamine, bisphenylenediamine, di-β-aminoethyl ether, diethylenetriamine, triethylenetetramine and di(β-aminoethoxy)- and di(β-aminopropoxy)-ethane. Further suitable polyamines are polymers and copolymers which may have additional amino groups in the side chain and oligoamides having amino terminal groups. Examples of such unsaturated amides are: methylene bisacrylamide, 1,6-hexamethylene bisacrylamide, diethylenetriamine trismethacrylamide, bis(methacrylamidopropoxy)ethane, β-methacrylamidoethyl methacrylate and N-[(β-hydroxyethoxy)ethyl]-acrylamide.

Suitable unsaturated polyesters and polyamides are derived, for example, from maleic acid and diols or diamines. The maleic acid may have been partially replaced by other dicarboxylic acids. They may be used together with ethylenically unsaturated comonomers, e.g. styrene. The polyesters and polyamides may also be derived from dicarboxylic acids and ethylenically unsaturated diols or diamines, especially from those having relatively long chains of e.g. from 6 to 20 carbon atoms. Examples of polyurethanes are those composed of saturated diisocyanates and unsaturated diols or unsaturated diisocyanates and saturated diols.

Aminoacrylates especially suitable as component (A)

There are especially suitable as component (A) acrylates that have been modified by reaction with primary or secondary amines, as is described, e.g., in US 3 844 916 by Gaske, in EP 280 222 by Weiss *et al.*, in US 5 482 649 by Meixner *et al.* or in US 5 734 002 by Reich *et al.*. Such amine-modified acrylates are also referred to as aminoacrylates. Aminoacrylates are obtainable, for example, from UCB Chemicals under the names EBECRYL 80, EBECRYL 81, EBECRYL 83 and EBECRYL 7100, from BASF under the names Laromer PO 83F, Laromer PO 84F and Laromer PO 94F, from Cognis under the names PHOTOMER 4775 F and PHOTOMER 4967 F, or from Cray Valley under the names CN501, CN503 and CN550.

The photopolymerisable compounds (A) can be used on their own or in any desired mixture.

Component (C)

The following are examples of special binders suitable as component (C):

1. surface coatings based on cold- or hot-crosslinkable alkyd, acrylate, polyester, epoxy or melamine resins or mixtures of such resins, optionally with the addition of a curing catalyst;
2. two-component polyurethane surface coatings based on hydroxyl-group-containing acrylate, polyester or polyether resins and aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;
3. two-component polyurethane surface coatings based on thiol-group-containing acrylate, polyester or polyether resins and aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;
4. one-component polyurethane surface coatings based on blocked isocyanates, isocyanurates or polyisocyanates which are deblocked during stoving; the addition of melamine resins is also possible, if desired;
5. one-component polyurethane surface coatings based on aliphatic or aromatic urethanes or polyurethanes and hydroxyl-group-containing acrylate, polyester or polyether resins;
6. one-component polyurethane surface coatings based on aliphatic or aromatic urethane acrylates or polyurethane acrylates having free amine groups in the urethane structure and melamine resins or polyether resins, optionally with the addition of a curing catalyst;
7. two-component surface coatings based on (poly)ketimines and aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;
8. two-component surface coatings based on (poly)ketimines and an unsaturated acrylate resin or a polyacetoacetate resin or a methacrylamidoglycolate methyl ester;
9. two-component surface coatings based on carboxyl- or amino-group-containing polyacrylates and polyepoxides;
10. two-component surface coatings based on anhydride-group-containing acrylate resins and a polyhydroxy or polyamino component;
11. two-component surface coatings based on acrylate-containing anhydrides and polyepoxides;
12. two-component surface coatings based on (poly)oxazolines and anhydride-group-containing acrylate resins or unsaturated acrylate resins or aliphatic or aromatic isocyanates, isocyanurates or polyisocyanates;
13. two-component surface coatings based on unsaturated (poly)acrylates and (poly)-malonates;
14. thermoplastic polyacrylate surface coatings based on thermoplastic acrylate resins or extrinsically crosslinking acrylate resins in combination with etherified melamine resins;

15. surface-coating systems, especially clearcoats, based on malonate-blocked isocyanates with melamine resins (e.g. hexamethoxymethylmelamine) as crosslinkers (acid-catalysed);
16. UV-curable systems based on oligomeric urethane acrylates and/or acylate acrylates, optionally with the addition of other oligomers or monomers;
17. dual-cure systems, which are cured first thermally and then by UV, or *vice versa*, the constituents of the surface-coating formulation containing double bonds that can be caused to react by UV light and photoinitiators and/or by electron-beam curing.

Further additives (C)

Depending on the intended application, the photopolymerizable mixtures may also, where appropriate, comprise further customary additives (C) in addition to the photoinitiator. Examples thereof are:
antioxidants, optical brighteners, fillers, thermal inhibitors, which are intended to prevent premature polymerization, e.g. 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl (4-hydroxy-TEMPO) and derivatives thereof;
antistatics, wetting agents or flow improvers and adhesion promoters;
thermally drying or curing catalysts, e.g. organometal compounds, amines or/and phosphines;
UV absorbers and light stabilisers, for example those from the group of the 2-(2'-hydroxyphenyl)-benzotriazoles, the 2-hydroxybenzophenones, esters of unsubstituted or substituted benzoic acids, acrylates, sterically hindered amines, oxalic acid diamides, 2-(2-hydroxyphenyl)-1,3,5-triazines, phosphites and phosphonites.

The following are examples of antioxidants, light stabilisers, UV absorbers and optical brighteners: RTMIRGANOX 1035, 1010, 1076, 1222, RTMTINUVIN P, 234, 320, 326, 327, 328, 329, 213, 292, 144, 622LD (available commercially from Ciba Specialty Chemicals), RTMANTIGENE P, 3C, FR, GA-80, RTMSUMISORB TM-061 (available commercially from Sumitomo Chemical Industries Co.), RTMSEESORB 102, 103, 501, 202, 712, 704 (available commercially from Sypro Chemical Co., Ltd.), RTMSANOL LS770 (available commercially from Sankyo Co. Ltd.) RTMUVITEX OB, available commercially from Ciba Specialty Chemicals.
Combined additives of sterically hindered piperidine derivatives (HALS) and sterically hindered phenols, for example additives of IRGANOX 1035 and TINUVIN 292, for example in a quantitative ratio of 1:1, are especially advantageous.

The photopolymerization may furthermore be accelerated by adding, as further additives (C), photosensitizers which shift or broaden the spectral sensitivity. Such photosensitizers are especially aromatic carbonyl compounds, such as benzophenone derivatives, thioxanthone derivatives, including especially isopropylthioxanthone, anthraquinone derivatives and 3-acylcoumarin derivatives, terphenyls, styryl ketones, and also 3-(aroylmethylene)-thiazolines, camphorquinone, and also eosine dyes, rhodamine dyes and erythrosine dyes.

The formulations may also comprise dyes and/or white or coloured pigments. Depending on the intended application, both inorganic and organic pigments may be used.

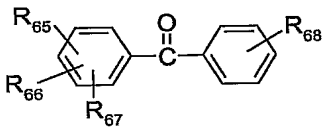
The above-described additives (C) are customary in the art and are accordingly used in the amounts customary in the art.

It is also possible to add solvents or water to the compositions used in the process of the invention. Suitable solvents are solvents that are known to the person skilled in the art, especially those customary in surface-coatings technology. Radiation-curable aqueous prepolymer dispersions are available commercially in many variations. Such a dispersion is to be understood as consisting of water and at least one prepolymer dispersed therein.

Further photoinitiators (D)

In certain cases, it may be advantageous to use mixtures of two or more of the photoinitiators according to the invention. Mixtures with known photoinitiators can, of course, also be used, for example mixtures with

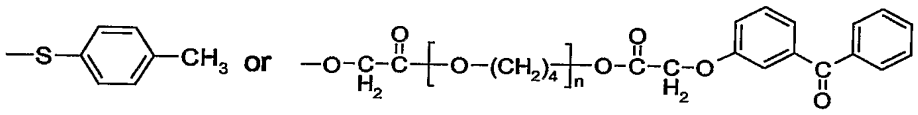
Benzophenones of the formula



wherein

R_{65}, R_{66} and R_{67} independently of one another are hydrogen, C_1-C_4-alkyl, C_1-C_4-halogenalkyl, C_1-C_4-alkoxy, chlorine or $N(C_1$-C_4-alkyl$)_2$;

R_{68} is hydrogen, C_1-C_4-alkyl, C_1-C_4-halogenalkyl, phenyl, $N(C_1$-C_4-alkyl$)_2$, $COOCH_3$,



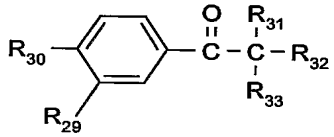
with n being 2-10.

Examples are:

ESACURE TZT® available from Lamberti, (a mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone).

Benzophenone, Darocur® BP

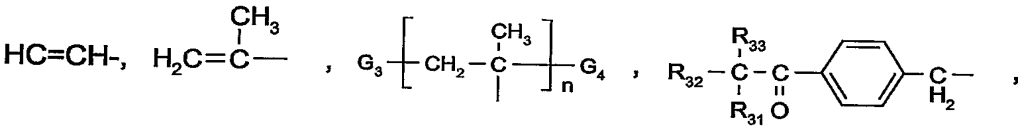
Alpha-hydroxyketones, alpha-alkoxyketones or alpha-aminoketones of the formula

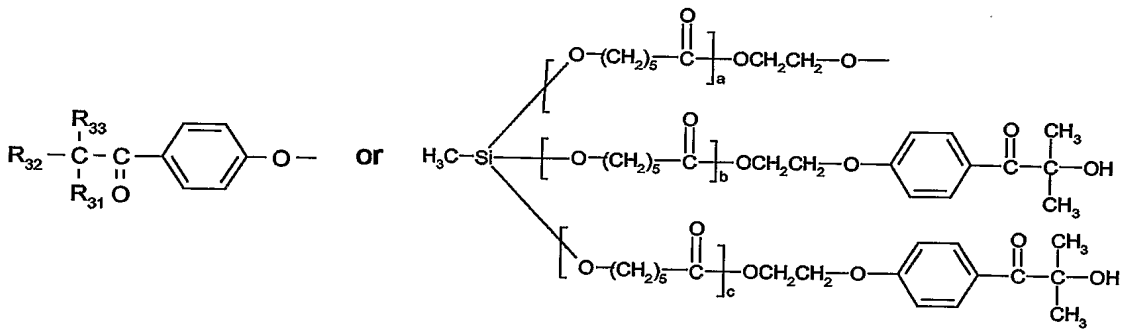


wherein

R_{29} is hydrogen or C_1-C_{18}-alkoxy;

R_{30} is hydrogen, C_1-C_{18}-alkyl, C_1-C_{18}-alkoxy, $-OCH_2CH_2-OR_{47}$, morpholino, SCH_3, a group -

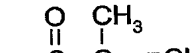




a, **b** and **c** are 1-3;

n is 2-10;

G_3 and G_4 independently of one another are end groups of the polymeric structure, preferably hydrogen or methyl;

R_{47} is hydrogen,  or  ;

R_{31} is hydroxy, C_1-C_{16}-alkoxy, morpholino, dimethylamino or -$O(CH_2CH_2O)_m$-C_1-C_{16}-alkyl;

R_{32} and R_{33} independently of one another are hydrogen, C_1-C_6-alkyl, C_1-C_{16}-alkoxy or -$O(CH_2CH_2O)_m$-C_1-C_{16}-alkyl; or unsubstituted phenyl or benzyl; or phenyl or benzyl substituted by C_1-C_{12}-alkyl; or R_{32} and R_{33} together with the carbon atom to which they are attached form a cyclohexyl ring; **m** is 1-20;

with the proviso that R_{31}, R_{32} and R_{33} not all together are C_1-C_{16}-alkoxy or -$O(CH_2CH_2O)_m$-C_1-C_{16}-alkyl.

Examples are:

1-Hydroxy-cyclohexyl-phenyl-ketone (IRGACURE®184) or IRGACUR® 500 (a mixture of IRGACURE®184 with benzophenone);

2-Methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one; (IRGACURE®907)

2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1; (IRGACURE®369)

1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one; (IRGACURE®2959)

2,2-Dimethoxy-1,2-diphenylethan-1-one (IRGACURE®651)

2-Hydroxy-2-methyl-1-phenyl-propan-1-one; (DAROCUR ® 1173)

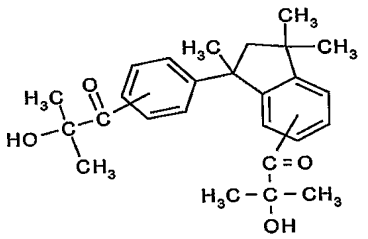
2-Dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one;

2-Benzyl-1-(3,4-dimethoxy-phenyl)-2-dimethylamino-butan-1-one;

2-Hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methyl-propan-1-one;

2-Hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one.

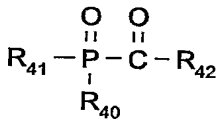
Another example of an alpha-hydroxy ketone is a compound of the formula



for example ESACURE KIP from Fratelli Lamberti, 2-hydroxy-1-{1-[4-(2-hydroxy-2-methyl-propionyl)-phenyl]-1,3,3-trimethyl-indan-5-yl}-2-methyl-propan-1-one.

Irgacure and Darocur products are available from Ciba Specialty Chemicals Inc.

Acylphosphine oxides of the formula



(V),

wherein

R_{40} and R_{41} independently of one another are unsubstituted C_1-C_{20}-alkyl, cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenylyl; or C_1-C_{20}-alkyl, cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenylyl substituted by halogen, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, C_1-C_{12}alkylthio or $NR_{52}R_{53}$, or R_{40} and R_{41} are independently of one another -(CO)R_{42}; wherein

R_{52} and R_{53} independently of one another are hydrogen, unsubstituted C_1-C_{12}-alkyl or C_1-C_{12}-alkyl substituted by OH or SH wherein the alkyl chain may be interrupted by one to four oxygen atoms; or R_{52} and R_{53} independently of one another are C_2-C_{12}-alkenyl, cyclopentyl, cyclohexyl, benzyl or phenyl;

R_{42} is unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenylyl, or cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenylyl substituted by halogen, C_1-C_4-alkyl and/or C_1-C_4-alkoxy; or R_{42} is a 5- or 6-membered heterocyclic ring having an S atom or N atom;

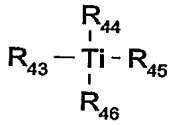
Examples are:

bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide; IRGACURE®819

2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide; Darocur® TPO

bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide.

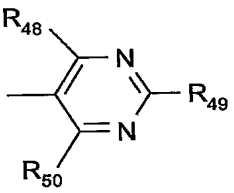
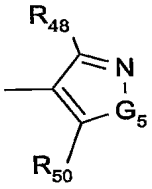
Titanocenes of the formula



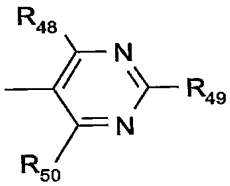
(VI),

R_{43} and R_{44} independently of one another are cyclopentadienyl optionally mono-, di-, or tri-substituted by C_1-C_{18}-alkyl, C_1-C_{18}-alkoxy, cyclopentyl, cyclohexyl or halogen;

R_{45} and R_{46} are phenyl having at least one F or CF_3 substituent in ortho position to the Ti-C bond and having at least a further substituent which is unsubstituted pyrrolinyl or polyoxaalkyl or which is pyrrolinyl or polyoxaalkyl substituted by one or two C_1-C_{12}-alkyl, di(C_1-C_{12}-alkyl)aminomethyl, morpholinomethyl, C_2-C_4-alkenyl, methoxymethyl, ethoxymethyl, trimethylsilyl, formyl, methoxy or phenyl; or

R_{45} and R_{46} are  or  ; wherein

G_5 is O, S, or NR_{51} with R_{51} being C_1-C_8alkyl, phenyl or cyclophenyl;

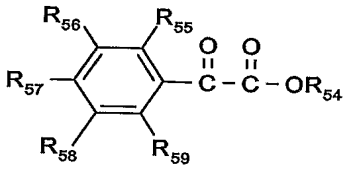
R_{48}, R_{49} and R_{50} independently of one another are hydrogen, halogen, C_2-C_{12}-alkenyl, C_1-C_{12}alkoxy, C_2-C_{12}-alkoxy interrupted by one to four oxygen atoms, cyclohexyloxy, cyclopentyloxy, phenoxy, benzyloxy, unsubstituted phenyl or biphenyl or phenyl or biphenyl substituted by C_1-C_4-alkoxy, halogen, phenylthio or C_1-C_4-alkylthio, with the proviso that R_{48} and R_{50} are not both hydrogen and that with respect to the residue  at least one substituent R_{48} or R_{50} is C_1-C_{12}alkoxy or C_1-C_{12}alkoxy interrupted by one to four oxygen atoms, cyclohexyloxy, cyclopentyloxy, phenoxy or benzyloxy.

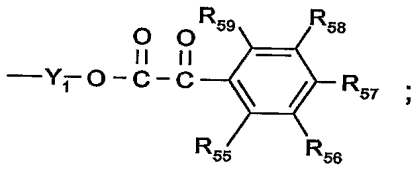
Examples are:

Bis(.eta.5-2,4-cyclopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl)-titanium IRGACURE® 784

Bis(2,6-difluorophenyl)bis[(1,2,3,4,5-eta)-1-methyl-2,4-cyclopentadien-1-yl]-titanium IRGACURE® 727

Phenylglyoxalates of the formula


(VII),

R_{54} is hydrogen, C_1-C_{12}-alkyl or a group  ;

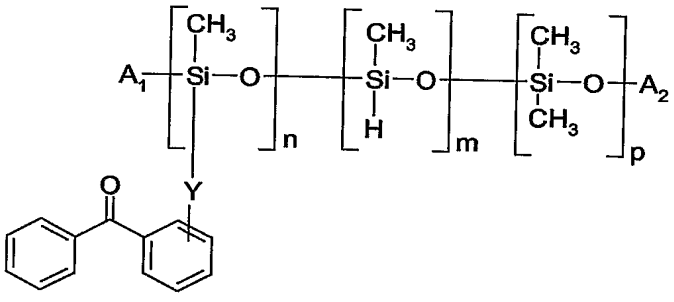
R_{55}, R_{56}, R_{57}, R_{58} and R_{59} independently of one another are hydrogen, unsubstituted C_1-C_{12}-alkyl or C_1-C_{12}-alkyl substituted by OH, C_1-C_4-alkoxy, phenyl, naphthyl, halogen or CN; and wherein the alkyl chain may be interrupted by one or more oxygen atoms; or R_{55}, R_{56}, R_{57}, R_{58} and R_{59} independently of one another are C_1-C_4-alkoxy, C_1-C_4-alkythio or $NR_{52}R_{53}$; R_{52} and R_{53} independently of one another are hydrogen, unsubstituted C_1-C_{12}-alkyl or C_1-C_{12}-alkyl substituted by OH or SH wherein the alkyl chain may be interrupted by one to four oxygen atoms; or R_{52} and R_{53} independently of one another are C_2-C_{12}-alkenyl, cyclopentyl, cyclohexyl, benzyl or phenyl.

Y_1 is C_1-C_{12}-alkylene optionally interrupted by one or more oxygen atoms.

An example is oxo-phenyl-acetic acid 2-[2-(2-oxo-2-phenyl-acetoxy)-ethoxy]-ethyl ester.

Surface-active photoinitiators

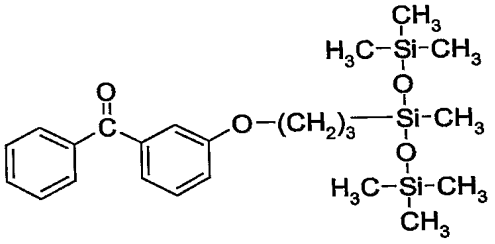
Surface-active benzophenones as described in WO 02/48204 of the formula



A_1 is methyl or $-O-Si(CH_3)_3$

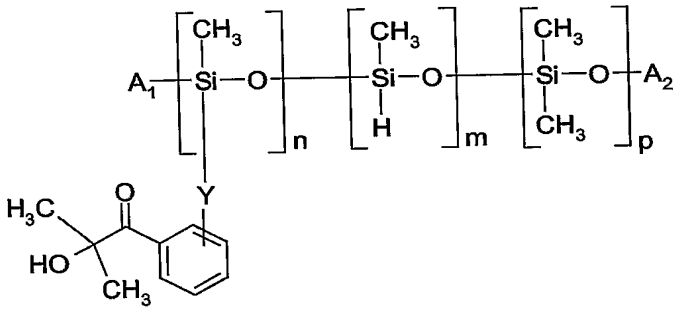
	A_2	is methyl or $-Si(CH_3)_3$;
	Y	is $-(CH_2)_a-$, $-(CH_2)_a-O-$, $-(CH_2)_b-O-(CH_2)_a-$ or $-(CH_2)_b-O-(CH_2)_a-O-$;
	a and b	are independently of one another 1-10;
	n	is a number from 1 to 10;
5	m	is a number from 0 to 25;
	p	is a number from 0 to 25.

An example is



10

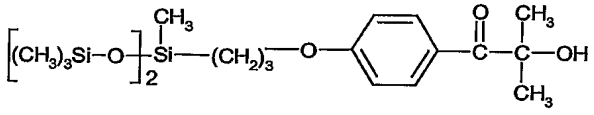
Siloxane-modified hydroxyketones as described in EP 1072326



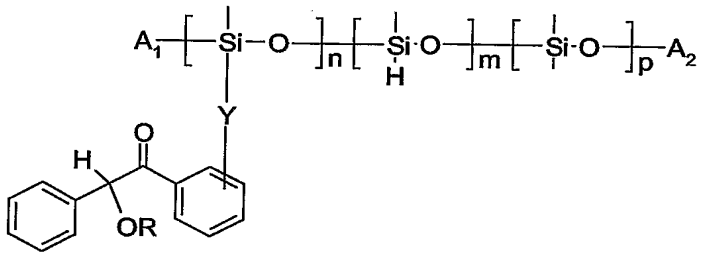
	A_1	is methyl or $-O-Si(CH_3)_3$
	A_2	is methyl or $-Si(CH_3)_3$;
15	Y	is $-(CH_2)_a-$, $-(CH_2)_a-O-$, $-(CH_2)_b-O-(CH_2)_a-$ or $-(CH_2)_b-O-(CH_2)_a-O-$;
	a and b	are independently of one another 1-10;
	n	is a number from 1 to 10;
	m	is a number from 0 to 25;
	p	is a number from 0 to 25.

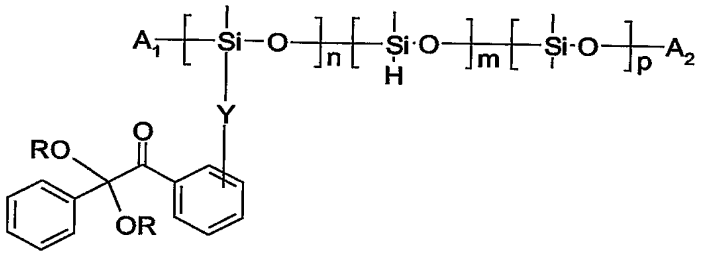
20

An example is



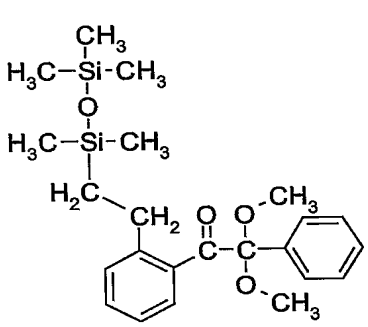
Surface-active benzil dialkyl ketals (BDK) or benzoins as described in WO 02/48203



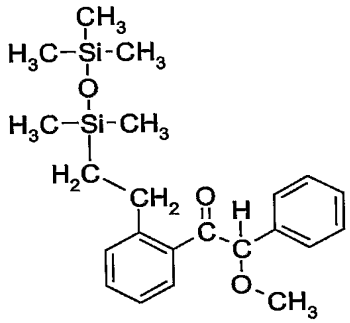


R	is H or C_1-C_4alkyl;
A_1	is methyl or –O-Si(CH_3)$_3$
A_2	is methyl or –Si(CH_3)$_3$;
Y	is $-(CH_2)_a-$, $-(CH_2)_a-O-$, $-(CH_2)_b-O-(CH_2)_a-$ or $-(CH_2)_b-O-(CH_2)_a-O-$;
a and b	are independently of one another 1-10;
n	is a number from 1 to 10;
m	is a number from 0 to 25;
p	is a number from 0 to 25.

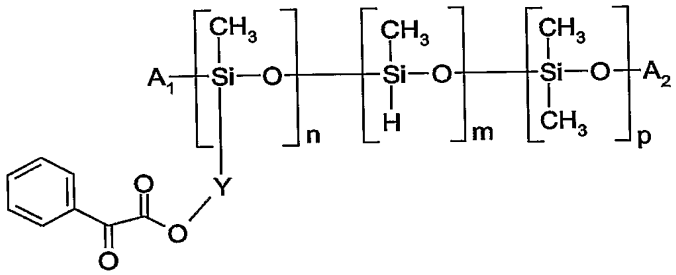
Examples are



or

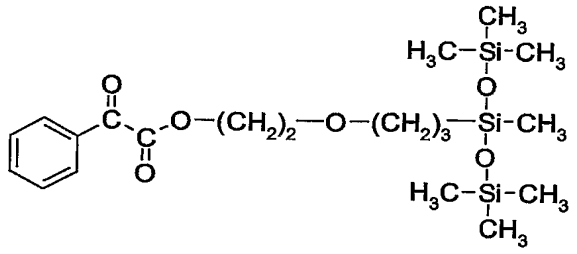


Monomeric and dimeric arylglyoxalic acid esters modified with siloxane *via* an ester group as described in WO 02/14439

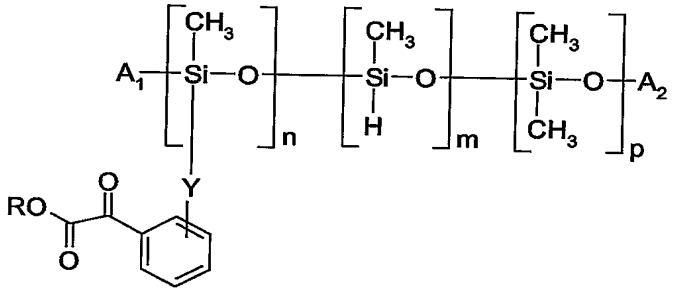


A_1	is methyl or $-O-Si(CH_3)_3$
A_2	is methyl or $-Si(CH_3)_3$;
Y	is $-(CH_2)_a-$, $-(CH_2)_a-O-$, $-(CH_2)_b-O-(CH_2)_a-$ or $-(CH_2)_b-O-(CH_2)_a-O-$;
a and b	are independently of one another 1-10;
n	is a number from 1 to 10;
m	is a number from 0 to 25;
p	is a number from 0 to 25.

An example is

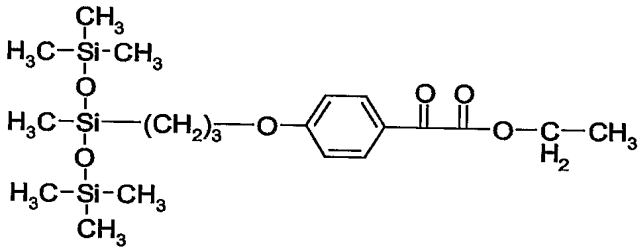


Monomeric and dimeric arylglyoxalic acid esters modified with siloxane *via* an aromatic group as described in WO 02/14326

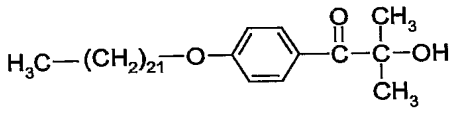


	R	is C_1-C_4alkyl;
	A_1	is methyl or $-O-Si(CH_3)_3$
10	A_2	is methyl or $-Si(CH_3)_3$;
	Y	is $-(CH_2)_a-$, $-(CH_2)_a-O-$, $-(CH_2)_b-O-(CH_2)_a-$ or $-(CH_2)_b-O-(CH_2)_a-O-$;
	a and b	are independently of one another 1-10;
	n	is a number from 1 to 10;
	m	is a number from 0 to 25;
15	p	is a number from 0 to 25.

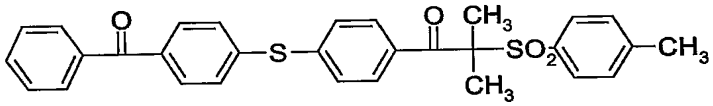
An example is



Long-chain-alkyl-modified hydroxyketones as described in WO 02/48202, for example 1-(4-docosyloxy-phenyl)-2-hydroxy-2-methyl-1-propanone



A further example of a photoinitiator is Esacure 1001 available from Lamberti: 1-[4-(4-benzoylphenylsulfanyl)phenyl]-2-methyl-2-(4-methylphenylsulfonyl)propan-1-one



It is also possible to add cationic photoinitiators, such as aromatic sulfonium, phosphonium or iodonium salts, such as are described, for example, in US 4 950 581, column 18, line 60 to column 19, line 10.

An example of an iodonium salt is (4-isobutyl-phenyl)-4-methylphenyl-iodonium hexafluoro-phosphate.

Maleimide derivatives may also be present, as described, e.g., in US 6 153 662 or US 6 150 431 by First Chemicals. N-(2-Trifluoromethylphenyl)maleimide and N-(2-*tert*-butyl-phenyl)maleimide may be mentioned by way of example.

The following may also be present: camphorquinones, acetophenones, 4-aroyl-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, e.g. benzil dimethyl ketal, peresters, e.g. benzophenonetetracarboxylic acid perester as described e.g. in EP 126 541; halomethyltriazines, e.g. 2-[2-(4-methoxyphenyl)-vinyl]-4,6-bistrichloromethyl[1,3,5]triazine, 2-(4-methoxyphenyl)-4,6-bistrichloromethyl-[1,3,5]triazine, 2-(3,4-dimethoxyphenyl)-4,6-bistrichloromethyl[1,3,5]triazine or 2-methyl-4,6-bistrichloromethyl[1,3,5]triazine, hexaarylbis-imidazole / coinitiator systems, e.g. ortho-chlorohexaphenyl bisimidazole together with 2-mercaptobenzothiazole, ferrocenium compounds or borate photoinitiators.

The photopolymerizable compositions contain the photoinitiator advantageously in an amount of from 0.05 to 15% by weight, preferably from 0.5 to 10% by weight, based on the

composition. The stated amount of photoinitiator relates to the sum of all of the photoinitiators added when mixtures thereof are used, i.e. either to the photoinitiator (B) or to the photoinitiators (B) + (D).

In addition, for certain applications it may be advantageous to add thermal radical initiators such as for example benzoyl peroxide (other suitable peroxides are described in US 4 950 581, column 19, lines 17-25).

Use

The photocurable compositions according to the invention are suitable for a variety of purposes, for example for overprint coatings, for inkjet inks, for printing inks, especially flexographic printing inks, for clearcoats, whitecoats or color-pigmented paint, for example for wood or metal, for powder coatings, as coating materials for substrates of all kinds, e.g. wood, textiles, paper, ceramics, glass, glass fibres, plastics, such as polyesters, polyethylene terephthalate, polyolefins or cellulose acetate, especially in the form of films, and also for metals, such as Al, Cu, Ni, Fe or Zn and GaAs, Si or SiO_2, to which a protective coating is to be applied or an image is to be applied by imagewise exposure.
Examples of coatings for metal include the application of a finish to metal sheets and tubes, cans or bottle closures, and topcoats for applications in the automobile industry
Examples of the photocuring of paper coatings are the application of a colourless finish to labels or book covers.

The photopolymerisable compositions can furthermore be used as daylight-curable paints for marking structures and roads, for photographic reproduction techniques, for holographic recording materials, for image recording processes or in the production of printing plates that can be developed using organic solvents or using aqueous alkaline media, for the production of masks for screen printing, as dental filling compounds, as adhesives, as pressure-sensitive adhesives, as laminating resins, as etch resists or permanent resists, both liquid and in the form of dry films, as photostructurable dielectrics, and as solder resists for electronic circuits, as resists in the production of color filters for any type of display screen, or in the creation of structures during the production of plasma displays and electroluminescent displays, in the production of optical switches, optical gratings (interference gratings), in the production of three-dimensional articles by bulk curing (UV curing in transparent moulds) or by the stereolithography process, as described, for example, in US 4 575 330, in the production of composite materials (e.g. styrene polyesters which may, where appropriate,

include glass fibres and/or other fibres and other adjuvants), and of fine layers (gel coats) and thick-layered compositions, in the coating or sealing of electronic components, or as coatings for optical fibres. The compositions are suitable, furthermore, for the production of optical lenses, e.g. contact lenses or Fresnel lenses, and also for the production of medical instruments, aids or implants.
The compositions may also be used to produce gels having thermotropic properties, such as are described, for example, in DE 197 00 064 and EP 678 534.

A preferred area of use is in overprint coatings. Typically, these consist of ethylenically unsaturated compounds, such as oligomeric and/or monomeric acrylates and aminoacrylates. Suitable compounds are listed under "compound (A)". The compounds and mixtures according to the invention are especially effective in overprint coatings of small layer thickness (5-10 μm).

A further preferred area of use is in UV-curable flexographic printing inks.
Such inks likewise consist of ethylenically unsaturated compounds (A) and comprise in addition UV flexographic resin/binder as well as further additives, such as flow agents and coloured pigments.

A further preferred area of use is in powder coatings. The powder coatings may be based on solid resins and monomers containing reactive double bonds (compounds (A)), e.g. maleates, vinyl ethers, acrylates, acrylamides and mixtures thereof. The powder coatings may also comprise binders, such as are described, for example, in DE 4 228 514 and EP 636 669. The UV-curable powder coatings may also comprise white or coloured pigments.

A further preferred area of use is in inkjet inks.

Inkjet inks contain a colorant.
A wide variety of organic and inorganic dyes and pigments, alone or in combination, may be selected for use in the inkjet ink compositions of this invention. The pigment particles should be sufficiently small (0.005 to 15 μm) to permit free flow of the ink at the ejecting nozzles. The pigment particles should preferably be 0.005 to 1 μm.

Very fine dispersions of pigments and their preparation are disclosed in e.g. US 5,538,548.

The pigment can be black, white, cyan, magenta, yellow, red, blue, green, brown, mixtures thereof, and the like. For example, suitable pigment materials include carbon blacks such as Regal 400R, Mogul L, Elftex 320 from Cabot Colo., or Carbon Black FW18, Special Black 250, Special Black 350, Special Black 550, Printex 25, Printex 35, Printex 55, Printex 150T from Degussa Co., and Pigment Black 7. Additional examples of suitable pigments are disclosed in, for example, U.S. 5,389,133.

Suitable white pigments are titanium dioxide (modifications rutile and anatas), e.g. KRONOS 2063 from Kronos, or HOMBITAN R610 L from Sachtleben.

Suitable pigments include, for instance, C. I. Pigment Yellow 17, C. I. Pigment Blue 27, C. I. Pigment Red 49:2, C. I. Pigment Red 81:1, C. I. Pigment Red 81:3, C. I. Pigment Red 81:x, C. I. Pigment Yellow 83, C. I. Pigment Red 57:1, C. I. Pigment Red 49:1, C. I. Pigment Violet 23, C. I. Pigment Green 7, C. I. Pigment Blue 61, C. I. Pigment Red 48:1, C. I. Pigment Red 52:1, C. I. Pigment Violet 1, C. I. Pigment White 6, C. I. Pigment Blue 15, C. I. Pigment Yellow 12, C. I. Pigment Blue 56, C. I. Pigment Orange 5, C. I. Pigment Black 7, C. I. Pigment Yellow 14, C. I. Pigment Red 48:2, C. I. Pigment Blue 15:3, C. I. Pigment Yellow 1, C. I. Pigment Yellow 3, C. I. Pigment Yellow 13, C. I. Pigment Orange 16, C. I. Pigment Yellow 55, C. I. Pigment Red 41, C. I. Pigment Orange 34, C. I. Pigment Blue 62, C. I. Pigment Red 22, C. I. Pigment Red 170, C. I. Pigment Red 88, C. I. Pigment Yellow 151, C. I. Pigment Red 184, C. I. Pigment Blue 1:2, C. I. Pigment Red 3, C. I. Pigment Blue 15:1, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C. I. Pigment Red 23, C. I. Pigment Red 112, C. I. Pigment Yellow 126, C. I. Pigment Red 169, C. I. Pigment Orange 13, C. I. Pigment Red 1-10, 12, C.I. Pigment Blue 1:X, C.I. Pigment Yellow 42, C.I. Pigment Red 101, C.I. Pigment Brown 6, C. I. Pigment Brown 7, C. I. Pigment Brown 7:X, C. I. Pigment Black 11, C. I. Pigment Metal 1, C. I. Pigment Metal 2, C.I. Pigment Yellow 128, C.I. Pigment Yellow 93, C.I. Pigment Yellow 74, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 154, C. I. Pigment Yellow 185, C.I. Pigment Yellow 180, C.I. Pigment Red 122, C.I. Pigment Red 184, and bridged aluminum phtalocyanine pigments, C. I. Pigment Red 254, C. I. Pigment Red 255, C.I. Pigment Red 264, C. I. Pigment Red 270, C.I. Pigment Red 272, C. I. Pigment Violet 19, C.I. Pigment Red 166, C.I. Pigment Red 144C. I. Pigment Red 202, C. I. Pigment Yellow 110, C. I. Pigment Yellow 128, C. I. Pigment Yellow 150, C. I. Pigment Orange 71, C. I. Pigment Orange 64, C. I. Pigment Blue 60.

The pigment may, but need not, be in the form of a dispersion comprising a dispersant, also called pigment stabilizer. The latter may be, for example, of the polyester, polyurethane or polyacrylate type, especially in the form of a high molecular weight block copolymer, and would typically be incorporated at 2.5% to 100% by weight of the pigment. An example of a polyurethane dispersant is EFKA 4047.

Further pigment dispersions are (UNISPERSE, IRGASPERSE) and ORASOL Dyes (solvent soluble dyes): C.I. Solvent Yellow 146, C.I. Solvent Yellow 88, C.I. Solvent Yellow 89, C.I. Solvent Yellow 25, C.I. Solvent Orange 11, C.I. Solvent Orange 99, C.I. Solvent Brown 42, C.I. Solvent Brown 43, C.I. Solvent Brown 44, C.I. Solvent Red 130, C.I. Solvent Red 233, C.I. Solvent Red 125, C.I. Solvent Red 122, C.I. Solvent Red 127, C.I. Solvent Blue 136, C.I. Solvent Blue 67, C.I. Solvent Blue 70, C.I. Solvent Black 28, C.I. Solvent Black 29

Especially emphazised are the MICROLITH-pigment preparations commercially available from Ciba Specialty Chemicals Inc. These pigment dispersions may be organic or inorganic pigments predispersed in a variety of resins, e.g. in vinyl resins, acrylic resins and aromatic polyurethane resins. MICROLITH-WA may for example be a line of pigments predispersed in alkaline water/alcohol soluble acrylic resin (specially developed for aqueous gravure and flexographic printing) with pigments that may be compatible with UV and inkjet printing inks.

The Microlith-K inkjet products are used in vinyl-based inks, which can be formulated to give good adhesion to many substrates, from plasticized and rigid PVC and metal foils, to polymer coated regenerated cellulose films.

Inkjet inks of the present invention may also more generally include other pigment preparations such as chips or in situ combination during grinding of pigments (as described above) and hyperdispersants (e.g.Solsperse as available from Avecia) into the binder carrier.

The substrates can be coated by applying a liquid composition, a solution or suspension to the substrate. The choice of solvent and the concentration are guided primarily by the nature of the composition and by the coating technique. The solvent should be inert, i.e. it should not enter into any chemical reaction with the components and it should be able to be removed again in the course of drying after coating. Examples of suitable solvents are ketones, ethers and esters, such as methyl ethyl ketone, isobutyl methyl ketone, cyclo-

pentanone, cyclohexanone, N-methylpyrrolidone, dioxane, tetrahydrofuran, 2-methoxy-ethanol, 2-ethoxyethanol, 1-methoxy-2-propanol, 1,2-dimethoxyethane, ethyl acetate, n-butyl acetate and ethyl 3-ethoxypropionate.

The formulation is applied uniformly to a substrate by means of known coating techniques, for example by spincoating, dipping, knife coating, curtain coating techniques, brush application, spraying, especially by electrostatic spraying, and reverse roll coating, and also by electrophoretic deposition. It is also possible to apply the photosensitive layer to a temporary flexible support and then to transfer the layer by lamination to the final substrate. Examples of methods of application can be found e.g. in Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A18, pp. 491-500.

The amount applied (layer thickness) and the nature of the substrate (layer support) are dependent on the desired field of application. The range of dry film thicknesses generally embraces values from about 0.1 μm to more than 100 μm.

The photosensitivity of the compositions of the invention generally ranges from about 200 nm into the NIR or IR region.

NIR (Near Infrared)-curing

The NIR radiation used in the process according to the invention is short-wave infrared radiation in the wavelength range from about 750 nm to about 1500 nm, preferably 750 nm to 1200 nm. Radiation sources for NIR radiation include, for example, conventional NIR radiation emitters, which are available commercially (for example, from Adphos).

IR-curing

The IR radiation used in the process according to the invention is medium-wave radiation in the wavelength range from about 1500 nm to about 3000 nm and/or longer-wave infra-red radiation in the wavelength range above 3000 nm.

IR radiation emitters of this kind are available commercially (for example, from Heraeus).

UV-curing

The photochemical curing step is carried out usually using light of wavelengths from about 200 nm to about 600 nm, especially from 200 to 450 nm. As light sources there are used a

large number of the most varied types. Both point sources and planiform projectors (lamp carpets) are suitable. Examples are: carbon arc lamps, xenon arc lamps, medium-, high- and low-pressure mercury lamps, optionally doped with metal halides (metal halide lamps), microwave-excited metal-vapor lamps, excimer lamps, super actinic fluorescent tubes, fluorescent lamps, argon filament lamps, electronic flash lamps, photographic flood lights, electron beams light emitting diodes (LED) and X-rays generated by means of synchrotrons or laser plasma.

As already mentioned, curing in the process of the invention may take place solely by exposure to electromagnetic radiation. Depending on the composition of the formulation to be cured, however, thermal curing before, during or after irradiation is advantageous.

Thermal curing takes place in accordance with methods known to the person skilled in the art. Curing is generally carried out in an oven, e.g. a circulating air oven, on a hotplate, or by irradiation using IR lamps. Curing without aids at room temperature is likewise possible, depending on the binder system used. The curing temperatures are generally from room temperature to 150°C, e.g. 25-150°C or 50-150°C. In the case of powder coatings or "coil coat" coatings, the curing temperatures may also be higher, e.g. up to 350°C.

The invention relates also to a method of producing a scratch-resistant durable surface, wherein a composition that either contains an ethylenically unsaturated compound and a photoinitiator of formula I, or contains an ethylenically unsaturated compound with an aminoacrylate and also contains a photoinitiator of formula I, II or III, is applied to a support; and curing of the formulation is carried out either solely by irradiation with electromagnetic radiation of a wavelength ranging from 200 nm into the NIR or IR region, or by irradiation with electromagnetic radiation and prior, simultaneous and/or subsequent action of heat.

The invention relates also to the use of the above-described composition and to a process for the production of pigmented and unpigmented surface coatings, overprint coatings, formulations for printing inks, inkjet inks, powder coatings, fine layers (gel coats), composite materials or glass fibre cable coatings.

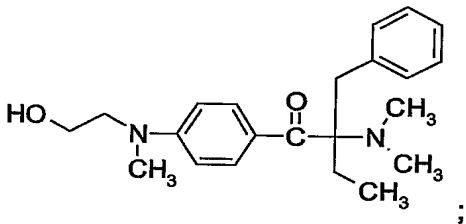
The invention further relates to the use of the compounds of formula I and II to prepare multifunctional photoinitiators with the proviso that the following compounds are excluded:

(A) at least one ethylenically unsaturated compound,

(B) a photoinitiator of formula I and/or II;

(C) optionally further binders or additives,

(D) optionally further photoinitiators or co-initiators, with the proviso that the following compounds are excluded:



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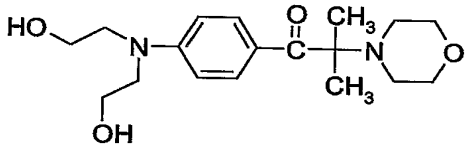
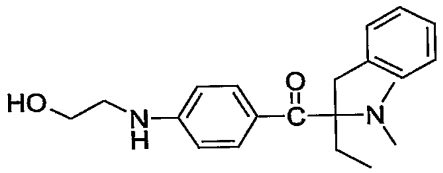


Examples:

Example 1:

Synthesis of 2-benzyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-butanone



1.1: 2-Benzyl-1-(4-fluorophenyl)-2-dimethylamino-1-butanone

This compound is prepared according to the procedure in EP-0284561-A2 (example 1 B).

1.2: 2-Benzyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-butanone

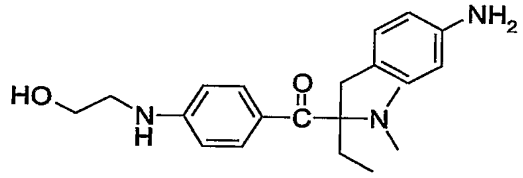
44.9 g (0.15 mol) 2-Benzyl-1-(4-fluorophenyl)-2-dimethylamino-1-butanone and 61.08 g (1.05 mol) ethanolamine are dissolved in 400 ml dimethylacetamide. 41.5 (0.3 mol) Potassium carbonate are added and the suspension is heated to 140°C while stirring. The reaction mixture is kept at this temperature during 16 hours, cooled to room temperature and diluted with water. The aqueous phase is several times extracted with ethyl acetate, the combined organic extracts washed with water and dried over magnesium sulfate. Evaporation of the solvent gives the crude product as a yellowish-brown oil. The product is purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate 2:1 → 1:1). The fractions containing the product are collected to give a slightly yellowish solid product. Recrystallisation from ethyl acetate/hexane gave 2-benzyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-butanone as slightly yellowish crystals melting at 109-111°C. Yield: 34.7 g (68%). ^{1}H-NMR data are in agreement with the proposed structure.

Elemental analysis: $C_{21}H_{28}N_2O_2$ (MG = 340.5)

	C %	H%	N%
calculated:	74.08	8.29	8.23
found:	73.95	8.42	7.99

Example 2

Synthesis of 2-[(4-aminophenyl)methyl]-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-butanone



2.1: 2-[(4-Nitrophenyl)methyl]-1-(4-fluorophenyl)-2-dimethylamino-1-butanone

2-Benzyl-1-(4-fluorophenyl)-2-dimethylamino-1-butanone, obtained as described for example 1.1, is added dropwise at 0-5°C to fuming nitric acid: After the addition, the reaction mixture is stirred for one hour and subsequently poured onto ice/water. The solution is extracted several times with methyl ethyl ketone, the organic extracts dried over magnesium sulfate and the solvent evaporated. The crude product is thus obtained as a brownish oil, which is purified by flash chromatography on silica gel using petroleum ether/ethyl acetate 4:1 as eluent. 2-[(4-Nitrophenyl)methyl]-1-(4-fluorophenyl)-2-dimethylamino-1-butanone is obtained as a yellowish oil that is used for the next step without further purification.

2.2: 2-[(4-Aminophenyl)methyl]-1-(4-fluorophenyl)-2-dimethylamino-1-butanone

7.0 g Palladium on charcoal (5%) are added to solution of 69,5 g (0.178 mol) 2-[(4-nitrophenyl)methyl]-1-(4-fluorophenyl)-2-dimethylamino-1-butanone in 700 ml ethanol in an hydrogenation autoclave. Hydrogen is entered with a continuous increase of pressure to 5 bar at temperature between room temperature and 40°C. After 25 hours no further hydrogen uptake is observed. The catalyst is filtered off and the crude product obtained as yellowish oil after evaporation of the solvent. Thin film chromatography shows a main product and some minor by-products. The crude material is used without further purification in the next reaction step.

2.3: 2-[(4-aminophenyl)methyl]-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-butanone

23.5 g (0.078 mol) 2-[(4-aminophenyl)methyl]-1-(4-fluorophenyl)-2-dimethylamino-1-butanone are reacted with ethanol amine (33.4 g, 0.55 mol) under conditions as described for example 1.2. The crude product obtained is purified by first by filtration over silica gel using hexane/ethyl acetate 1:1 → ethyl acetate as the eluent, followed by flash chromatography on silica gel (eluant: ethyl acetate). 10.2 g (37%) 2-[(4-aminophenyl)methyl]-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-butanone are obtained as a viscous yellow oil.

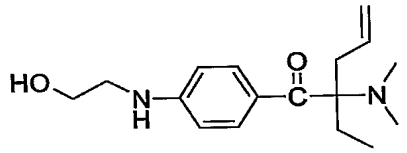
^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 8.3 (d, 2H-C(2')/C(6')); 7.0 (d, 2H-C(2''') and C(6''')); 6.62 (d, 2H-C(3''') and C(5''')); 6.53 (d, 2H-C(3')/C(5')); 3.83 (t, 2H-C(8')); 3.33 (t, 2H-C(7')); 3.07 (broad s, 2NH); 2.95 (d, 2H-C(1''')); 2.36 (s, 6H (CH_3-N)); 2.02 (m, 1H-(C(1''); 1.81 (m, 1H-(C(1''); 0.71 (t, 3H-C(2'').

Elemental analysis: $C_{21}H_{29}N_3O_2$ (MG = 355.48)

	C %	H%	N%
calculated:	70.95	8.22	11.82
found:	69.11	8.51	11.22

Example 3:

Synthesis of 2-ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-pent-4-en-1-one



3.1: 1-(4-Fluorophenyl)-2-dimethylamino-1-butanone

This compound is prepared according to the procedure in EP-02845610-A2 (example 1 A).

3.2. 2-Ethyl-1-(4-fluorophenyl)-2-dimethylamino-pent-4-en-1-one

76 g (0.363 mol) 1-(4-Fluorophenyl)-2-dimethylamino-1-butanone are dissolved in 300 ml methyl ethyl ketone. While stirring at room temperature, 48.3 g (0.4 mol) 1-bromo-prop-2-ene are added over one hour to give a beige suspension. The reaction mixture is stirred for 18 hours at room temperature and then heated to 70°C. At this temperature 29.05 g (0.73 mol) powdered sodium hydroxide are added. The reaction mixture turns orange and is subsequently cooled to room temperature. The mixture is diluted with water and dichloro-methane. The organic phase is separated, dried over magnesium sulfate and the solvent evaporated. The crude product thus obtained is purified by flash chromatography on silica gel, using petroleum ether/ethyl acetate as the eluent. 2-Ethyl-1-(4-fluorophenyl)-2-dimethyl-amino-pent-4-en-1-one is obtained as a yellowish liquid. Yield: 56.9 g (63%). ^{1}H-NMR data are in agreement with the proposed structure.

3.3: 2-Ethyl-1-[4-(2-hydroxyethyamino)phenyl]- 2-dimethylamino-pent-4-en-1-one

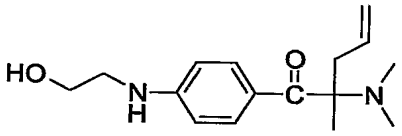
24.9 g (0.1 mol) 2-Ethyl-1-(4-fluorophenyl)-2-dimethylamino-pent-4-en-1-one are reacted with ethanol amine under conditions as described for example 1.2. The crude product is obtained as yellowish liquid, which is further, purified by chromatography on silica gel using petroleum

ether/ethyl acetate as eluent. The fractions containing the product are collected and the compound recrystallized from hexane. 2-Allyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethyl-amino-1-butanone (16.2 g, 56%) is obtained as slightly yellowish crystals with a melting point of 90-92°C. %). ^{1}H-NMR data are in agreement with the proposed structure.

^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 8.3 (d, 2H-C(2')/C(6')); 6.54 (d, 2H-C(3')/C(5')); 5.94 (m, H-C(4)); 5.07 (dxd, 1 H-C(5); 4.98 (dxd, 1H-C(5)); 3.87 (t, 2H-C(8'); 3.37 (t, 2H-C(7')); 2.7-2.5 (m, 2H-C(3)); 2.44 (s, 6H (CH_3-N)); 2.15-1.8 (m, 3H, 2H-(C(1") and OH); 0.73 (t, 3H-C(2").

Example 4:

Synthesis of 1-[4-(2-hydroxyethyamino)phenyl]-2-methyl-2-dimethylamino-1-pent-4-en-1-one

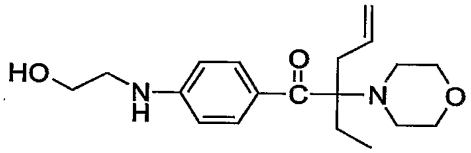


This compounds is prepared by the same procedure as Example 2, except that 1-(4-fluorophenyl)-2-dimethylamino-1-propanone is used as the starting material.

^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 8.43 (d, 2H-C(2')/C(6')); 6.54 (d, 2H-C(3')/C(5')); 5.54 (m, H-C(4)); 4.90 (dxd, 1 H-C(5); 4.87 (dxd, 1H-C(5)); 3.87 (t, 2H-C(8'); 3.37 (t, 2H-C(7')); 2.75 (dxd, 1H-C(3)); 2.40 (dxd. 1H-C(3)); 2.26 (s, 6H (CH_3-N)); 1.74 (broad s, OH); 1.17 (s, 3H-C(1").

Example 5:

Synthesis of 2-ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-(morpholin-4-yl)-1-pent-4-en-1-one



5.1 1-(4-Fluorophenyl)-2-(morpholin-4-yl)-1-butanone

85.3 g (0.98 mol) morpholine are dissolved in 200 ml tetrahydrofurane and cooled to 0°C. 100 g (0.41 mol) 1-(4-Fluorophenyl)-2-bromo-1-butanone (obtained according to the process described in EP-A-3002) in 200 ml tetrahydrofurane are added dropwise to this solution at 0°C. The reaction mixture is then heated to 50°C during 16 hours before cooling to room

temperature. The mixture is poured into water and extracted several times with ethyl acetate. The organic phase is dried with magnesium sulfate and the solvent evaporated in vacuo. 1-(4-Fluorophenyl)-2-(morpholin-4-yl)-1-butanone (102 g, 99%) is thus obtained as a brownish liquid, the structure being confirmed by ^{1}H-NMR analysis. The crude product is used without further purification for the next reaction step.

5.2 2-Ethyl-1-(4-fluorophenyl)-2-(morpholin-4-yl)-pent-4-en-1-one

56 g of a 50% suspension of sodium hydride in mineral oil (0.22 mol sodium hydride) is added to 100 ml dimethylformamide. 45.2 g (0.16 mol) 1-(4-Fluorophenyl)-2-(morpholin-4-yl)-1-butanone, dissolved in 50 ml diemethylformamide, are added to this suspension dropwise and at room temperature, and subsequently stirred overnight. Then, 19.36 g 1-brom-2-propene are added dropwise. The temperature raises to 50°C and the solution is kept at this temperature for 16 hours. After cooling, excess sodium hydride is destroyed by the addition of 5 ml isopropanol and the reaction mixture subsequently poured onto an ice/water mixture. The organic products are extracted with ethyl acetate, the combined extracts dried over magnesium sulfate and the solvent evaporated. The crude product thus obtained is purified by chromatography silica gel (eluent: ethyl acetate/petroleum ether 4:1). 2-Ethyl-1-(4-fluorophenyl)-2-(morpholin-4-yl)-pent-4-en-1-one (17.8 g, 38%) is obtained as a yellowish oil. ^{1}H-NMR analysis is in agreement with the proposed structure. This compound is used for the next step.

5.3. 2-Ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-(morpholin-4-yl)-1-pent-4-en-1-one

11.4 g (0.04 mol) 2-Ethyl-1-(4-fluorophenyl)-2-(morpholin-4-yl)-pent-4-en-1-one are reacted with 17.1 g (0.28 mol) ethanolamine under conditions as described for example 1.2. The crude product is purified by chromatography on silica gel using petroleum ether/ethyl acetate 2:3 as eluent. Pure 2-ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-(morpholin-4-yl)-1-pent-4-en-1-one (3.6 g, 27%) is obtained as a yellowish viscous oil.

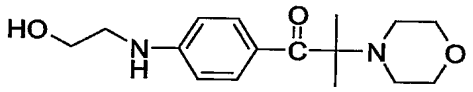
^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 8.41 (d, 2H-C(2')/C(6')); 6.52 (d, 2H-C(3')/C(5')); 5.92 (m, H-C(4)); 5.08 (dxd, 1 H-C(5); 5.02 (dxd, 1H-C(5)); 4.77 (broad s, OH); 3.84 (t, 2H-C(8'); 3.62 (7. 4H-C(2''') and C(6'''); 3.34 (broad t, 2H-C(7')); 2.9-2.85 (m, 2H-C(3)); 2.25-2.10 (m, 4H-C(3''') and C(5'''); 2.10-1.85 (m, 2H-C(1'')); 0.72 (t, 3H_C(2'')).

Elemental analysis: $C_{19}H_{28}N_2O_5$ (MG = 332.44)

	C %	H%	N%
calculated:	68.65	8.49	8.43
found:	68.32	8.58	8.37

Example 6:

Synthesis of 1-[4-(2-hydroxyethyamino)phenyl]-2-methyl-2-(morpholin-4-yl)-1-propanone



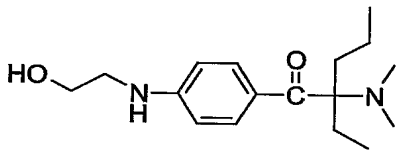
9.6 g (0.03 mol) 1-(4-fluorophenyl)-2-(morpholin-4-yl)-1-propanone (prepared as described in DE 19753655-A1, example 1b) are reacted with 12.85 g (0.21 mol) ethanolamine under conditions as described for example 1.2. The crude product is purified by chromatography on silica gel using petroleum ether/ethyl acetate 1:2 as eluent. The fractions containing the product are collected and the brownish crystals recrystallized from hexane/ethyl acetate 4:1. Pure 1-[4-(2-hydroxyethyamino)phenyl]-2-methyl-2-(morpholin-4-yl)-1-propanone (5.1 g, 58%) is obtained as beige crystals with a melting point of 77-78°C.

Elemental analysis: $C_{16}H_{24}N_2O_3$ (MG = 292.4)

	C %	H%	N%
calculated:	65.73	8.27	9.58
found:	65.82	8.31	9.72

Example 7:

Synthesis of 2-ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-pentan-1-one



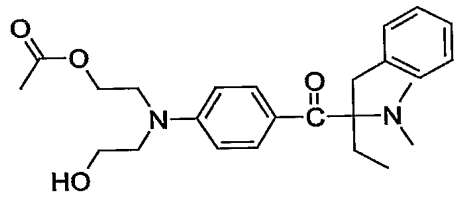
10.1 g 2-Allyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-butanone are dissolved in 100 ml ethyl acetate. After addition of 1 g Pd/carbon 5%, the reaction mixture is treated with hydrogen at normal pressure until an uptake of 0.78 l H_2 (100%) is reached. After filtration of the catalyst the solvent is evaporated. The crude product is recrystallized from hexane to give 6.8 g (67%) 2-ethyl-1-[4-(2-hydroxyethyamino)phenyl]-2-dimethylamino-1-pentan-1-one as a slightly yellowish solid with a melting point of 74-77°C.

Elemental analysis: $C_{17}H_{28}N_2O_2$ (MG = 292.4)

	C %	H%	N%
calculated:	69.83	9.65	9.58
found:	69.99	9.52	9.53

Example 8:

Synthesis of 2-Benzyl-2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-1-butanone



8.1: 1-{[4-[Bis(2-hydroxyethyl)amino]phenyl}-1-butanone

49.5 g (0.3 mol) 1-(4-Fluorophenyl)-1-butanon and 315.4 g (3.0 mol) are heated in a steel autoclave under a pressure of 8-10 bar to 200°C during 100 hours. After cooling the reaction mixture is poured on ice/water, the organic phase is separated and the water phase extracted several times with ethyl acetate. The organic extracts are dried over magnesium sulfate and the solvent evaporated. The brownish crude product is filtered over silica gel using ethyl acetate/petroleum ether as eluent. 1-{[4-[Bis(2-hydroxyethy)amino]phenyl}-1-butanone is obtained as a solid which is recrystallized in ethyl acetate/hexane 7:2 to give the product as a beige solid with a melting point of 72-75°C.

8.2: 1-{[4-[Bis(2-acetoxyethyl)amino]phenyl}-2-bromo-1-butanone

34.9 g (0.138 mol) 1-{[4-[Bis(2-hydroxyethy)amino]phenyl}-1-butanone are dissolved in 500 ml acetic acid. The solution is saturated with gaseous hydrogen chloride and subsequently cooled to 0-5°C. 22.2 g (0.138 mol) bromine are added at this temperature over 90 minutes. The reaction mixture is subsequently stirred over night at room temperature. After heating under a stream of nitrogen, the reaction mixture is poured slowly into 550 ml of 30% sodium hydroxide solution. Extraction with ethyl acetate, followed by drying over magnesium sulfate and evaporation of the solvent gives 55 g 1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-2-bromo-1-butanone as a brownish liquid.

^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 7.91 (d, 2H-C(2')/C(6')); 6.77 (d, 2H-C(3')/C(5')); 5.05 (t, H-C(2)); 4.27 (t, 42H-C(2")); 3.69 (t, 4H-C(1")); 2.16 (txd, 2H-C(3)); 2.05 (s. 6H CH_3CO); 1.05 (t, 3H-C(4)).

8.3: 2-Dimethylamino-1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-1-butanone

25 g (0.06 mol) 1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-2-bromo-1-butanone are added dropwise to 25 g of a 33% solution of dimethylamine in ethanol (0.18 mol dimethylamine) at 0°C. The reaction mixture is stirred over night at room temperature, after which the solvent subsequently is evaporated in vacuum. 20.0 g (88%) 2-Dimethylamino-1-{[4-[bis(2-acetoxy-

ethyl)amino]phenyl}-1-butanone are obtained as a yellowish liquid which is used in the next reaction step without further purification.

^{1}H NMR (ppm; TMS = 0 ppm as internal standard); 7.98 (d, 2H-C(2')/C(6')); 6.77 (d, 2H-C(3')/C(5')); 4.27 (t, 4H-C(2")); 3.80 (m, H-C(2)); 3.71 (t, 4H-C(1")); 2.32 (s, 6H CH_3-N); 2.05 (s. 6H CH_3CO); 1.72 (txd, 2H-C(3)); 0.85 (t, 3H-C(4)).

8.4.: 2-Benzyl-2-dimethylamino-1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-1-butanone

To a solution of 12.5 g 2-dimethylamino-1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-1-butanone in 25 ml methyl ethyl ketone, 5.64 g (0.033 mol) benzyl bromide are added dropwise. The reaction mixture is heated to 70°C during four hours. Then, 2.64 g (0.066 mol) powdered sodium hydroxide are added and the mixture heated for another two hours. After cooling, the reaction mixture is diluted with water and ethyl acetate. The organic phase is separated, dried over magnesium sulfate and the solvent evaporated to give a yellowish viscous liquid. This crude reaction mixture is purified by chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as the eluent. A first fraction isolated consists of 8.4 g 2-Benzyl-2-dimethylamino-1-{[4-[bis(2-acetoxyethyl)amino]phenyl}-1-butanone, obtained as a yellowish oil.

Elemental analysis: $C_{27}H_{36}N_2O_5$ (MG = 468.59)

	C %	H%	N%
calculated:	69.21	7.74	5.98
found:	69.40	8.13	5.49

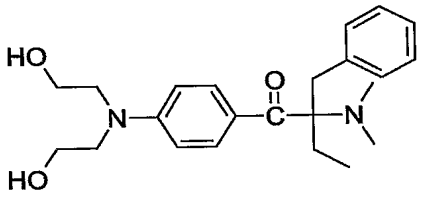
8.5.: 2-Benzyl-2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-1-butanone

A second fraction from the chromatography described under 8.4 contains 3.4 g 2-benzyl-2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-1-butanone as a yellowish oil.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.34 (d, 2H-C(2')/C(6')); 7.21 (m. 5H, benzylic protons); 6.68 (d, 2H-C(3')/C(5')); 4.31 (t, 2H-C(2")-$OCOCH_3$); 3.84 (t, 2H-C(2")-OH); 3.70 (t, 2H-C(1")-CH_2OCOCH_3); 3.61 (t, 2H-C(1")-CH_2OH); 3.18 (dxd, 2H-C(1'); 2.34 (s, 6H CH_3-N); 2.02 (s. 3H CH_3CO); 2.05 and 1.85 (m, 2H-C(3)); 0.68 (t, 3H-C(4)).

Example 9:

Synthesis of 2-benzyl-1-{[4-[bis(2-hydroxyethy)amino]phenyl}-2-dimethylamino-1-butanone



3.4 g (0.008 mol) 2-Benzyl-2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-1-butanone, obtained according to example 8.5., are suspended in water and treated with powdered sodium hydroxide at 70°C and then at reflux. After five hours, the reaction mixture is cooled to room temperature and extracted with ethyl acetate. The organic solution is dried over magnesium sulfate and the solvent evaporated. 1.7 g (55%) 2-benzyl-1-{[4-[bis(2-hydroxyethy)amino]phenyl}-2-dimethylamino-1-butanone are obtained as yellowish oil after chromatography on silicagel using petroleum ether/ethyl acetate as eluent.

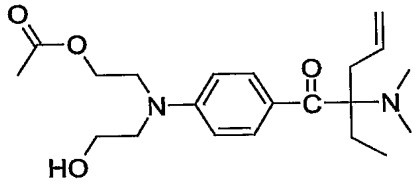
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.33 (d, 2H-C(2')/C(6')); 7.21 (m. 5H, benzylic protons); 6.59 (d, 2H-C(3')/C(5')); 3.88 (t, 4H-C(2")); 3.64 (t, 4H-C(1")); 3.18 (dxd, 2H-C(1'); 2.34 (s, 6H CH_3-N); 2.05 and 1.85 (m, 2H-C(3)); 0.68 (t, 3H-C(4)).

Elemental analysis: $C_{23}H_{32}N_2O_3$ (MG = 384.52)

	C %	H%	N%
calculated:	71.84	8.39	7.29
found:	71.11	8.54	6.91

Example 10:

Synthesis of 2-dimethylamino-1-{[4-(2-acetoxyethyl-2-hydroxyethyl-amino)-phenyl}-2-ethyl-1-pent-4-en-1-one



This compound is prepared analogous to the procedure described for example 8, except that allyl bromide is used instead of benzyl bromide in step 8.4. The compound is obtained as a yellowish viscous oil.

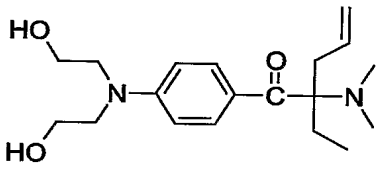
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.34 (d, 2H-C(2')/C(6')); 6.67 (d, 2H-C(3')/C(5')); 5.94 (m, 1H, H-C(4)); 5.06 (dxd, 1H H-C(5)); 4.99 (dxd, 1H, H-C(5)); 4.30 (t, 2H-C(2")-$OCOCH_3$); 3.84 (t, 2H-C(2")-OH); 3.71 (t, 2H-C(1")-CH_2OCOCH_3); 3.61 (t, 2H-C(1")-CH_2OH); 2.64 (m, 2H-C(3); 2.41 (s, 6H CH_3-N); 2.04 (s. 3H CH_3CO); 2.05 and 1.85 (m, 2H-C(1')); 0.68 (t, 3H-C(2')).

Elemental analysis: $C_{21}H_{32}N_2O_4$ (MG = 376.50)

	C %	H%	N%
calculated:	66.99	8.57	7.44
found:	66.63	8.56	6.86

Example 11:

Synthesis of 2-dimethylamino-1-{[4-[bis(2-hydroxyethy)amino]-phenyl}-2-ethyl-1-pent-4-en-1-one



This compound is prepared analogous to the procedure described for example 9, except that the compound of example 10 is used as starting material. The compound is obtained as a yellowish viscous oil.

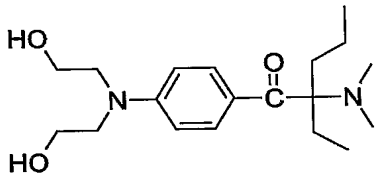
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.33 (d, 2H-C(2')/C(6')); 6.57 (d, 2H-C(3')/C(5')); 5.90 (m, 1H, H-C(4)); 5.06 (dxd, 1H H-C(5)); 4.99 (dxd, 1H, H-C(5)); 3.85 (t, 4H-C(2")); 3.62 (t, 4H-C(1")); 2.64 (m, 2H-C(3); 2.40 (s, 6H CH_3-N); 2.02 and 1.86 (m, 2H-C(1')); 0.70 (t, 3H-C(2')).

Elemental analysis: $C_{19}H_{30}N_2O_3$ (MG = 334.46)

	C %	H%	N%
calculated:	68.23	9.04	8.38
found:	67.63	9.33	7.80

Example 12:

Synthesis of 2-dimethylamino-1-{[4-[bis(2-hydroxyethy)amino]-phenyl}-2-ethyl-1-pentan-1-one



This compound is prepared analogous to the procedure described for example 7, except that the compound of example 11 is used as starting material for the hydrogenation. The compound is obtained as a yellowish viscous oil.

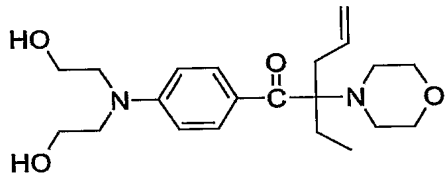
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.29 (d, 2H-C(2')/C(6')); 6.57 (d, 2H-C(3')/C(5')); 3.85 (t, 4H-C(2")); 3.62 (t, 4H-C(1")); 2.40 (s, 6H CH_3-N); 1.85 (m, 4H, 2H-C(3) and 2H-C(1')); 1.15 (m, 2H-C(4)); 0.85 (t, 3H-C(5)); 0.78 (t, 3H-C(2')).

Elemental analysis: $C_{19}H_{32}N_2O_3$ (MG = 336.47)

	C %	H%	N%
calculated:	67.82	9.59	8.33
found:	66.85	9.54	7.75

Example 13:

Synthesis of Synthesis of 1-{[4-[bis(2-hydroxyethy)amino]-phenyl}-2-ethyl-2-morpholin-4-yl)-1-pent-4-en-1-one



This compound is prepared analogous to the procedure described for example 11, except that in the amination step morpholine is used in stead of dimethylamine. The compound is obtained as a yellowish viscous oil.

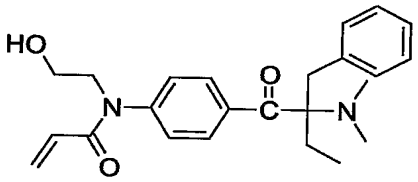
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 7.98 (d, 2H-C(2')/C(6')); 6.68 (d, 2H-C(3')/C(5')); 5.85 (m, 1H, H-C(4)); 5.25 (dxd, 1H H-C(5)); 5.18 (dxd, 1H, H-C(5)); 4.0-3.55 (4 m, 14H, 4H-C(2"), 4H-C(1"), 4H-C(2'"/6'") and 2H-C(3)); 2.60 (m, 4H-C(3'"/5'")); 1.90 and 1.75 (m, 2H-C(1')); 0.85 (t, 3H-C(2')).

Elemental analysis: $C_{21}H_{32}N_2O_4$ (MG = 376.47)

	C %	H%	N%
calculated:	66.99	8.57	7.44
found:	66.78	8.62	7.24

Example 14:

Synthesis of 2-benzyl-1-{4-[(2-hydroxyethyl)-acryloyl-amino]phenyl}-2-dimethylamino-1-butanone



6.0 g (0.018 mol) 2-Benzyl-1-[4-(2-hydroxyethylamino)phenyl]-2-dimethylamino-1-butanone (example 1) is dissolved in 50 ml methyl ethyl ketone and cooled to 0-5°C. A solution of 1.4 g sodium hydroxide in 5 ml water is added, followed by the dropwise addition of 1.8 g acryloyl chloride. When the addition is complete, the reaction mixture is stirred for an additional 10 minutes and poured in water. The organic phase is separated, dried over magnesium sulfate and the solvent evaporated in vacuo. The brownish oil obtained is purified by chromatography on silica gel, using petroleum ether/ethyl acetate as eluent. A first fraction (2.0 g) conconsists according to ^{1}H-NMR-analysis of 60% 2-benzyl-1-{4-[(2-acryloyloxyethyl)-amino]phenyl}-2-dimethylamino-1-butanone and 40% 2-benzyl-1-{4-[(2-acryloyloxyethyl)-acryloyl-amino]phenyl}-2-dimethylamino-1-butanone.

A second fraction (2.0 g) is pure 2-benzyl-1-{4-[(2-hydroxyethyl)-acryloyl-amino]phenyl}-2-dimethylamino-1-butanone.

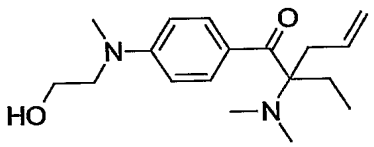
^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.38 (d, 2H-C(2')/C(6')); 7.3-7.1 (m, 2H-C(3')/C(5') and 5 benzylic protons); 6.42 (dxd, 1H, H-C(3'")); 6.05 (dxd, 1H H-C(3'")); 5.61 (dxd, 1H, H-C(2'")); 4.0 (t, 2H-C(2")); 3.82 (t, 2H-C(1"); 3.20 (m, 2H-C(1')); 2.38 (s, 6H, CH3-N); 2.10 and 1.82 (m, 2H-C(3)); 0.71 (t, 3H-C(4)). The IR spectrum (KBr) shows an amide band at 1670 cm^{-1}.

Elemental analysis: $C_{24}H_{30}N_2O_3$ (MG = 394.52)

	C %	H%	N%
calculated:	73.07	7.67	7.10
found:	73.60	8.45	6.26

Example 15:

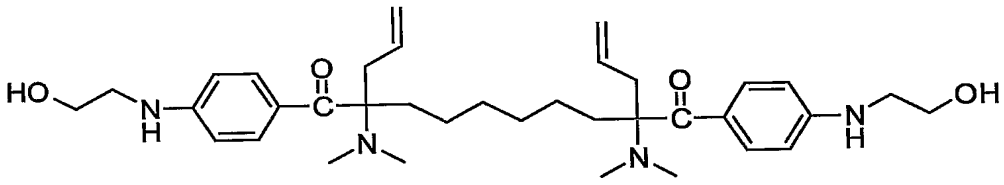
Synthesis of 2-Dimethylamino-2-ethyl-1-{4-[(2-hydroxy-ethyl)-methyl-amino]-phenyl}-pent-4-en-1-one



In a 300 ml sulfonation under argon atmosphere, 2.90 g (10 mmol) of 2-dimethylamino-2-ethyl-1-[4-(2-hydroxy-ethylamino)-phenyl]-pent-4-en-1-one are dissolved in 55 ml THF and 137 ml acetonitrile. 4.5 ml (60 mmol) of a 37% aqueous formaldehyde solution are added over 10 min. at 25°C, followed by 2.21 g (30 mmol) of sodium cyanoborohydride. After 10 min at 25°C, the mixture is stirred at 50°C for 4h, cooled to room temperature and diluted with 100 ml water. The yellow semi-solid is redissolved in methylene chloride, washed with 20 ml of aq. sat. $NaHCO_3$ and water, the organic phase dried with brine and sodium sulfate, and evaporated under vacuum to give 2.3 g (75%) of the title compound as a yellow oil. ^{1}H-NMR ($CDCl_3$, 400 MHz); [ppm]: 8.30 (d, 2H), 6.66 (d, 2H), 5.85-5.96 (m, 1H), 5.01-5.11 (m, 2H), 3.85 (t, 2H), 3.58 (t, 2H), 3.08 (s, 3H), 2.64-2.75 (m, 2H), 2.47 (s, 6H), 1.91-2.07 (m, 2H), 0.73 (t, 3H).

Example 16:

Synthesis of 2,8-diallyl-2,8-bis-dimethylamino-1.9-bis-[4-(2-hydroxy-ethylamino)-phenyl]-nonane-1,9-dione



16.1.: 1.9-Bis-(4-fluoro-phenyl)-nonane-1,9-dione

To a suspension of 32.0 g $AlCl_3$ in 290 ml fluorobenzene, 25 g azealic acid dichloride is added at 0-10°C while stirring. The reaction mixture was stirred over night and subsequently hydrolysed with dilute hydrogen chloride. After extraction with dichloromethane, drying over magnesium sulfate and evaporation of the solvent, 37.4 g 1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are obtained as a yellowish liquid.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.00 (m, 2H-C(2')/C(6')); 7.15 (m, 2H-C(3')/C(5')); 2.94 (t, 4H-C(2) and C(8)); 1.73 (m, 4H-C(3) and C(7)); 1.40 (m, 6H-C(4), C(5) and C(6)).

16.2.: 2,8-Dibromo-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione

37.4 g (0.11 mol) 1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are brominated with 35.16 g (0.22 mol) bromine under conditions analogous to those described in example 8.2. 57.9 g 2,8-Dibromo-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are obtained, which are used for the next reaction step without further purification.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.07 (m, 2H-C(2')/C(6')); 7.20 (m, 2H-C(3')/C(5')); 5.06 (t, 2H-C(2) and C(8)); 2.18 (m, 4H-C(3) and C(7)); 1.51 (m, 6H-C(4), C(5) and C(6)).

16.3.: 2,8-dimethylamino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione

30.2 g 2,8-Dibromo-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are reacted with 5.6 mol dimethylamine under the conditions described for example 8.3. 23.9 g 2,8-dimethylamino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are obtained as yellowish viscous oil.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.09 (m, 2H-C(2')/C(6')); 7.08 (m, 2H-C(3')/C(5')); 3.82 (m, 2H-C(2) and C(8)); 2.29 (6H, CH_3-N); 1.8 and 1.6 (2 m, 4H-C(3) and C(7)); 1.35-1.10 (m, 6H-C(4), C(5) and C(6)).

16.4.: 2,8-Diallyl-2,8-dimethylamino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione

12.9 g 2,8-Dimethylamino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione (30 mmol) are reacted with 7.98 g (66 mmol) allyl bromide under the conditions described for example 3.2. 8.66 g (57%) 2,8-Diallyl-2,8-dimethylamino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione are obtained as a viscous yellowish oil, which is purified by chromatography on silica gel (eluent: hexane/ethyl acetate 9:1.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.36 (m, 2H-C(2')/C(6')); 7.00 (m, 2H-C(3')/C(5')); 5.82 (m, 2H-C(2'/2")); 4.99 (dxd, 2H-C(3'/3")); 4.96 (d, 2H-C(3'/3")); 2.55 (m, 2H-C(2) and C(8)); 2.36 (6H, CH_3-N); 1.8 and 1.65 (2 m, 4H-C(3) and C(7)); 1.15-0.75 (m, 6H-C(4), C(5) and C(6)).

16.5.: 2,8-Diallyl-2,8-bis-dimethylamino-1.9-bis-[4-(2-hydroxy-ethylamino)-phenyl]-nonane-1,9-dione

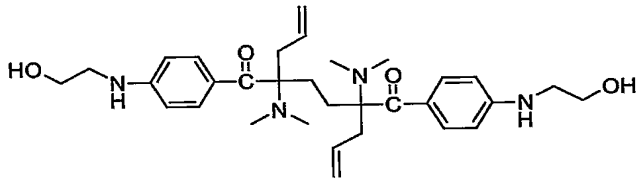
9.16 g Ethanolamine (0.15 mol) are reacted with 5.7 g (0.01 mol) 2,8-diallyl-2,8-dimethyl-amino-1.9-bis-(4-fluoro-phenyl)-nonane-1,9-dione in dimethylacetamide under the conditions described for example 1.2. After isolation, the crude product is purified by chromatography on silica gel using isopropanole/dichloromethane and then ethanol/dichloromethane as the

eluent. 3.8 g (64%) 2,8-Diallyl-2,8-bis-dimethylamino-1.9-bis-[4-(2-hydroxy-ethylamino)-phenyl]-nonane-1,9-dione are obtained as a very viscous yellowish oil.

^{1}H-NMR (ppm; TMS = 0 ppm as internal standard); 8.26 (d, 2H-C(2')/C(6')); 6.51 (d, 2H-C(3')/C(5')); 5.88 (m, 2H-C(2'/2")); 4.99 (dxd, 2H-C(3'/3")); 4.95 (d, 2H-C(3'/3")); 3.85 (m, 4H, 2H-C(2") and 2H-C(2"')); 3.36 (m, 4H, 2H-C(1") and 2H-C(1"')); 2.55 (m, 2H-C(2) and C(8)); 2.35 (6H, CH_3-N); 2.0-1.65 (m, 4H-C(3) and C(7)); 1.205-0.70 (m, 6H-C(4), C(5) and C(6)).

Example 17:

Synthesis of 2,5-diallyl-2,5-bis-dimethylamino-1.6-bis-[4-(2-hydroxy-ethylamino)-phenyl]-hexan-1,6-dione

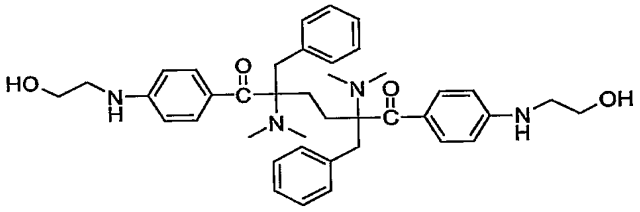


This compound is prepared following the process described for example 15. except that adipoyl dichloride is used in step 15.1. instead of azealic

The compound is obtained as a yellowish solid with a melting point of 95-96°C.

Example 18:

Synthesis of 2,5-dibenzyl-2,5-bis-dimethylamino-1.6-bis-[4-(2-hydroxy-ethylamino)-phenyl]-hexan-1,6-dione



This compound is prepared following the process described for example 16. except that benzyl bromide instead of allyl bromide.

The compound is obtained as a yellowish solid with a melting point of 126-127°C.

Application Example

Example 19: Curing of a blue offset printing ink on white paper

A photocurable blue offset printing ink is preapared in accordance with the following formulation:

18.3 g of Ebecryl ®1608 (UCB, Belgium)

18.3 g of Ebecryl ® 657 (polyester acrylate from UCB, Belgium)

20.0 g of Ebecryl ® 220 (urethane acrylate from UCB, Belgium)

20.9 g of Ebecryl ® 150 (bisphenol A derivative diacrylate from UCB, Belgium)

22.5 g Irgalit blue GLO (Cu-phthalocyanine pigment from Ciba Specialty Chemicals)

The above components are grounded down to a stock paste. Portions of the stock paste are mixed with the photoinitiators indicated in the table (% by weight on the stock paste). The solubility of the initiator in the formulation is rated as good (+), acceptable (±) or bad (+) and the results shown in Table 1.

The blue printing ink thus obtained is applied with 1.5 g/m^2 (~1.5 µm thickness) on white paper using a Prüfbau laboratory printing equipment. The samples are exposed in an irradiation apparatus with a 80 W/cm mercury lamp (IST). The rate of passage of the sample through the irradiation apparatus is thereby increased continuously until adequate curing no longer occurs. The maximum rate at which the ink still passes the properties test for surface cure and through cure is shown in Table 1. The odor of the cured film is rated on a scale from 1 (odorless) to 3 (strong odor).

photoinitiator	conc (%)	solubility	curing rate (m/min) for surface cure	curing rate (m/min) for through cure	odor
Compound of example 1	3.0	+	100	120	1
	4.0	+	140	170	1
Irgacure 369	3.0	-	70	110	1
	4.0	-	90	130	1
Irgacure 907	4.0	1	80	90	2-3

The results show that the compound of example 1 is more efficient as a photoinitiator than the reference compounds while being equal or better soluble and odorless.

Example 20: Curing of a blue offset printing ink on a white polyethylene foil

A photocurable blue offset printing ink is prepared in accordance with the following formulation:

26.9 g of IRR 440 (flexo basic resin)

19.0 g of OTA 480 (acrylated trifunctional resin , UCB, Belgium)

18.0 g of Ebecryl ® 645 (modified diacrylate of Bisphenol A epoxy resin diluted with 25% of TPGDA , from UCB, Belgium)

13.0 g of HDDA (1,6-hexanediol diacrylate)

10.0 g of Ebecryl ® 220 (urethane acrylate from UCB, Belgium)

1.3 g of Ebecryl ® 168 (methacrylated acidic compound from UCB, Belgium)

0.7 g of DC 57 (Leveling agent)

11.1 g Irgalit blue GLO (Cu-phthalocyanine pigment from Ciba Specialty Chemicals)

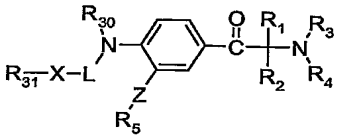
The above components are grounded down to a stock paste. Portions of the stock paste are mixed with the photoinitiators indicated in the table (% by weight on the stock paste). The solubility of the initiator in the formulation is rated as good (+), acceptable (±) or bad (+) and the results shown in Table 2.

The blue printing ink thus obtained is applied with 1.38 g/cm^2 1.5 µm thickness on a corona treated white polyethylene foil using a Prüfbau laboratory printing equipment. The samples are exposed in an irradiation apparatus with a 120 W/cm mercury lamp (IST). The rate of passage of the sample through the irradiation apparatus is thereby increased continuously until adequate curing no longer occurs. The maximum rate at which the ink still passes the properties test for surface cure and through cure is shown in Table 1. The adhesion of the cured film to the foil is measure by the Tesa tape test.

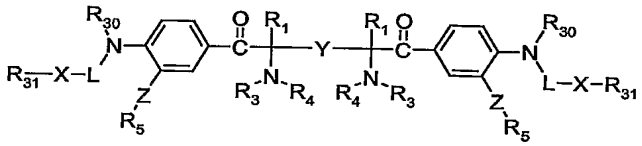
photoinitiator	conc (%)	solubility	curing rate (m/min) for surface cure	curing rate (m/min) for through cure	adhesion
Compound of example 1	6.0	+	200	40	+
Irgacure 369	6.0	+	170	90	50

Claims

1. Photoinitiators of formula I or II



I



II

wherein

L is a linker;

X is -O-, -S- or -NR_{32}-;

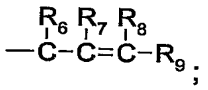
Y is a direct bond, C_1-C_{16}-alkylene, cyclohexylene, xylylene, dihydroxyxylylene, C_4-C_8-alkenediyl, C_6-C_{10}-alkadienediyl or dipentenediyl;

Z is a direct bond, -CH_2-, -O-, -S- or -NR_{10}-;

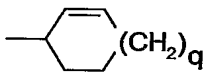
R_1 and R_2 are independently of each other either

(a) linear or branched C_1-C_{12}-alkyl, which is unsubstituted or substituted by one or more of the groups C_1-C_4-alkyoxy, phenoxy, halogen or phenyl;

(b) a radical of the formula

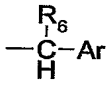


(c) a radical of the formula



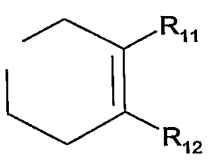
where q is 0, 1, 2 or 3; or

(d) a radical of the formula

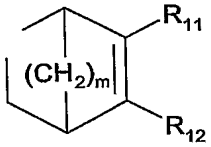


where Ar is phenyl, which is unsubstituted or substituted by one or more of the groups halogen, OH, NO_2, -$N(R_{10})_2$, C_1-C_{12}-alkyl, C_1-C_4-alkyl that is additionally substituted by OH, halogen, $N(R_{10})_2$, C_1-C_{12}-alkoxy, -$COO(C_1$-C_{18}-alkyl), -$CO(OCH_2CH_2)_nOCH_3$ or -$OCO(C_1$-C_4-alkyl); C_1-C_{12}-alkyoxy, C_1-C_4-alkyoxy that is additionally substituted by -$COO(C_1$-C_{18}-alkyl) or -$CO(OCH_2CH_2)_nOCH_3$; -$OCO(C_1$-C_4-alkyl), C_1-C_8-alkylthio, phenoxy, -$COO(C_1$-C_{18}-alkyl), -$CO(OCH_2CH_2)_nOCH_3$, phenyl or benzoyl; where n is 1-20; or

R^1 together with R^2 forms a ring of the formula



or



where m is 1 or 2;

R_3 is hydrogen, C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, -COO(C_1-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl or C_7-C_9-phenylalkyl;

R_4 is C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, -COO(C_1-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl; or R_4 and R_2 together is C_1-C_7-alkylene, C_7-C_{10}-phenylalkylene, o-xylylene, 2-butenylene or C_2-C_3-oxa- or azaalkylene; or R_4 and R_3 together is C_3-C_7-alkylene that may be interrupted by -O-, -S-, -CO- or -N(R_{13})- and substituted by hydroxy, C_1-C_4-alkoxy or -COO(C_1-C_4-alkyl);

R_5 is hydrogen or C_1-C_4-alkyl; or R_5 together with R_{30} is C_1-C_2-alkylene;

R_6 is hydrogen, C_1-C_8-alkyl or phenyl;

R_7, R_8 and R_9 independently of each other are hydrogen or C_1-C_4-alkyl, or R_7 and R_8 together are C_3-C_7-alkylene;

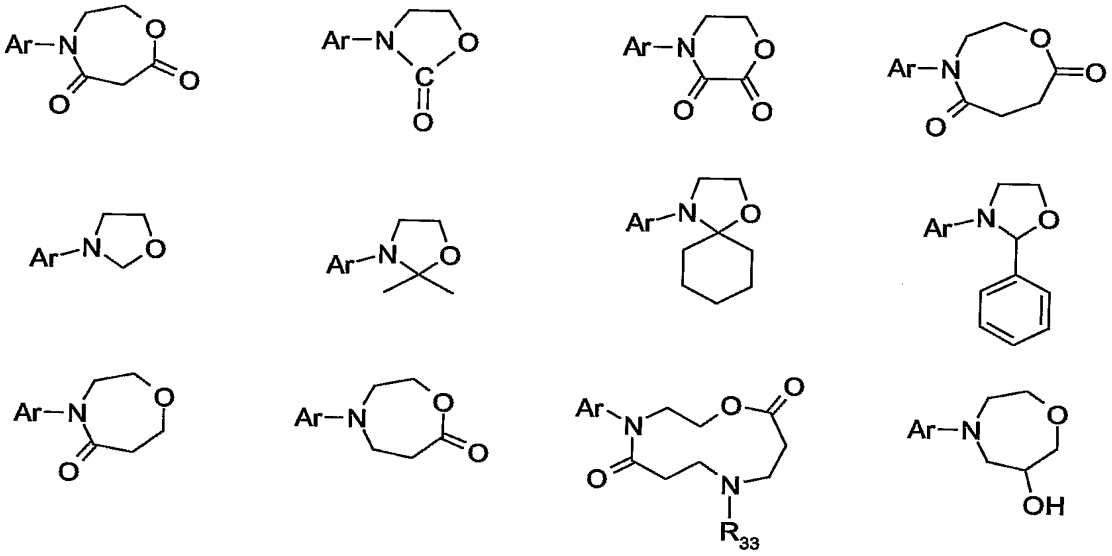
R_{10} is hydrogen, C_1-C_8-alkyl, C_3-C_5-alkenyl, C_7-C_9-phenlyalkyl, C_1-C_4-hydroxyalkyl or phenyl;

R_{11} and R_{12} independently of each other are hydrogen or C_1-C_4-alkyl, or R_{11} and R_{12} together are C_3-C_7-alkylene;

R_{13} is hydrogen, C_1-C_{12}-alkyl, which may be interrupted by one or more -O- or C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, -CH_2CH_2CN, -CH_2CH_2COO(C_1-C_4-alkyl), C_2-C_8-alkanoyl, or benzoyl;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -$NR_{33}R_{34}$, -SR_{35}, -COOH or -COO(C_1-C_4-alkyl); or benzoyl or norbornenoyl substituted by hydroxy, or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl; or

R_{30} and R_{31} together with the group –N-L-X form cyclic structures selected from



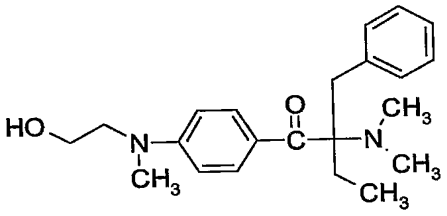
R_{32} is hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); .. C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl benzoyl or norbornenoyl substituted by hydroxy, C_1-C_4-alkoxy, -$NR_{33}R_{34}$, -SR_{35}, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl;

R_{33} and R_{34} independently of one another are hydrogen, C_1-C_{12}-alkyl, C_2-C_4-hydroxy-alkyl, C_3-C_{10}-alkoxyalkyl, C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl, C_2-C_{18}-alkanoyl or benzoyl; or R_{33} and R_{34} together are C_2-C_8-alkylene optionally interrupted by -O-, -S- or -NR_{36}- , or are C_2-C_8-alkylene optionally substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl);

R_{35} is C_1-C_{18}-alkyl, hydroxyethyl, 2,3-dihydroxypropyl, cyclohexyl, benzyl, phenyl, C_1-C_{12}-alkylphenyl, -CH_2-COO(C_1-C_{18}-alkyl), -CH_2CH_2-COO(C_1-C_{18}-alkyl) or -$CH(CH_3)$-COO(C_1-C_{18}-alkyl);

R_{36} is hydrogen, C_1-C_{12}-alkyl optionally interrupted by one or more no adjacent –O-atoms, C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, -CH_2CH_2CN, -CH_2CH_2COO(C_1-C_4-alkyl), C_2-C_{12}-alkanoyl or benzoyl.

with the proviso that the following compounds are excluded: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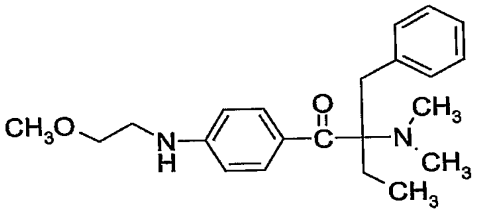
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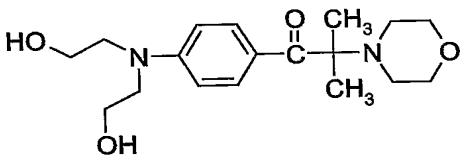
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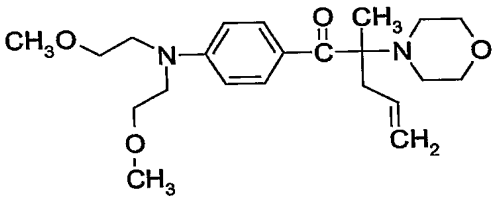
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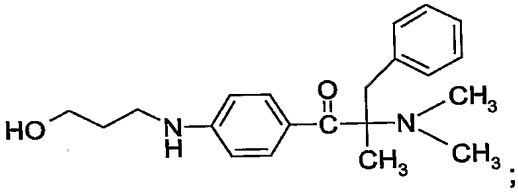
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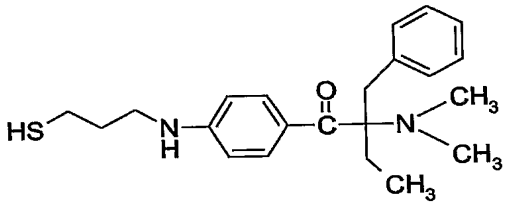
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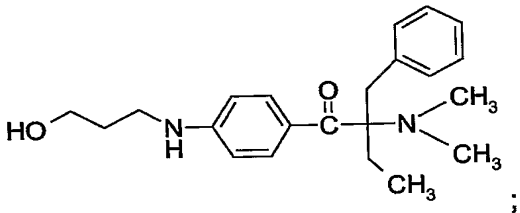
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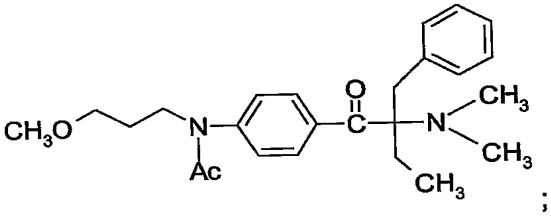
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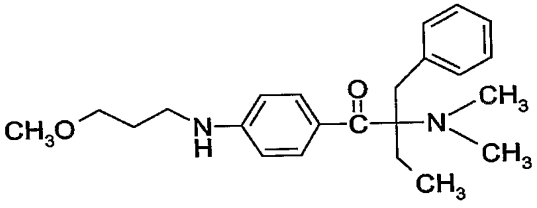

;

2. Photoinitiators according to claim 1, wherein

L is a linker;

X is –O-, -S- or –NR_{32}-

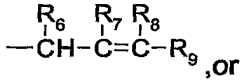
Y is C_1-C_8-alkylene;

Z is a direct bond;

R_1 and R_2 are independently of each other either

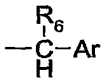
(a) linear or branched C_1-C_{12}-alkyl;

(b) a radical of the formula;



,or

(c) a radical of the formula



wherein Ar is phenyl, which is unsubstituted or substituted by one or more of the groups NO_2, -$N(R_{10})_2$, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylthio, phenoxy;

R_3 is C_1-C_4-alkyl, C_2-C_4-alkyl substituted by hydroxy, C_1-C_4-alkoxy; C_3-C_5-alkenyl;

R_4 independently of R_3 has one of the meanings of R_3; or R_4 together with R_3 is C_4-C_5-alkylene that may be interrupted by -O-, -$N(R_{13})$-;

R_5 is hydrogen;

R_6, R_7, R_8 and R_9 independently of each other are hydrogen or methyl;

R_{10} is hydrogen, C_1-C_4-alkyl or C_3-C_5-alkenyl;

R_{13} is hydrogen or C_1-C_4-alkyl;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl); allyl, cyclohexyl or C_7-C_9-phenylalkyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl; or -CO-NH-C_1-C_{12}-alkyl or –CO-NH-(C_0-C_{12}-alkylen)-N=C=O, optionally interrupted by one or two phenylene,methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-Isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl;

R_{32} is hydrogen or C_1-C_{12}-alkyl.

3. Photoinitiators according to claim 2, wherein

L is linear or branched C_2-C_{18}-alkanediyl;

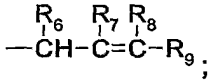
X is –O-; Y is C_1-C_6-alkylene;

Z is a direct bond;

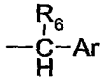
R_1 and R_2 are independently of each other either

(a) linear or branched C_1-C_3-alkyl;

(b) a radical of the formula;



(c) a radical of the formula



where Ar is phenyl, which is unsubstituted or substituted by CH_3-, NO_2 or -$N(R_{10})_2$;

R_3 is methyl,

R_4 is methyl or R_4 together with R_3 is C_5-alkylene that is interrupted by -O-;

R_5 is hydrogen;

R_6, R_7, R_8 and R_9 are hydrogen;

R_{10} is hydrogen;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy; C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or C_3-C_5-alkenoyl.

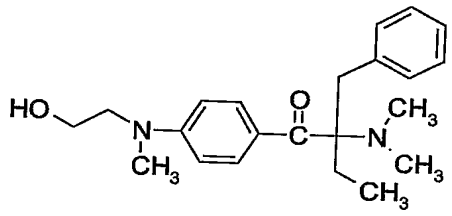
4. A composition comprising

(A) at least one ethylenically unsaturated compound;

(B) a photoinitiator of formula I and/or II;

(C) optionally further binders or additives;

(D) optionally further photoinitiators or co-initiators, with the proviso that the following compounds are excluded: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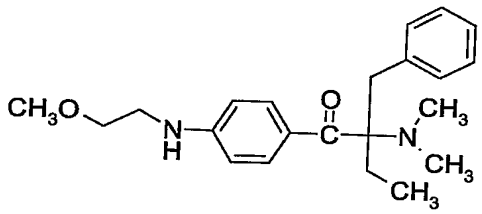
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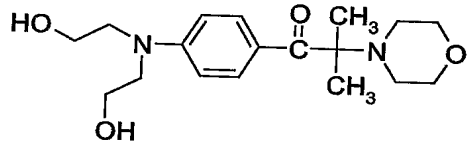
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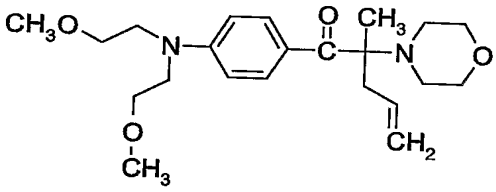
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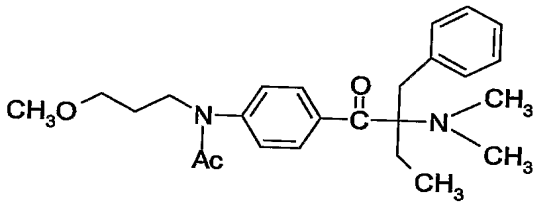
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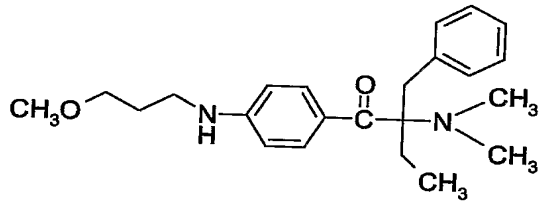

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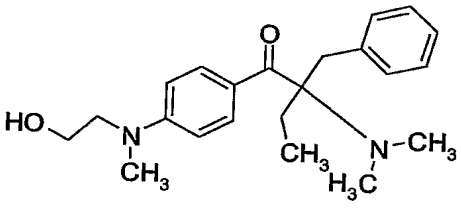
5. The use of compounds of the formula I and/or II as defined in claim 1 as photoinitiators to cure compositions according to claim 4.

10 6. The use of compounds of the formula I or II as defined in claim 1 to prepare multifunctional photoinitiators with the proviso that the following compounds are excluded: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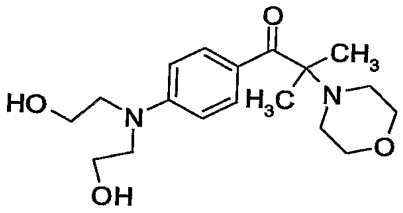
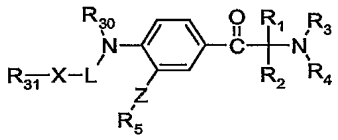


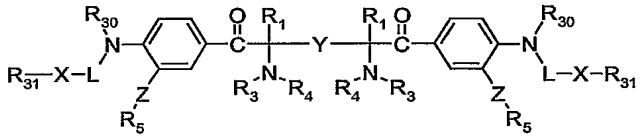
15

Abstract

The invention relates to novel photoinitiators of formula I or II



I



II

wherein each of the substituents is given the definition as set forth in the Specification and claims.

The photoinitiators can be used to prepare multifunctional photoinitiators.